HALO-CONTAINING ANION EXCHANGE MEMBRANES AND METHODS THEREOF

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ABSTRACT
The present invention relates to functionalized polymers including a poly(phenylene) structure having modifications suitable for an anion exchange membrane. Exemplary modifications include use of a cationic moiety and a halo moiety. Methods and uses of such structures and polymers are also described herein.

20 Claims, 31 Drawing Sheets
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FIG. 2B

FIG. 2C
FIG. 8

(when $a = h$, $R^{R_2}$ are present, and $R^{R_3} = R^f$)
FIG. 9A
FIG. 11
FIG. 17A
FIG. 17B
FIG. 18A
FIG. 18C

FIG. 19A
FIG. 22

- \( \text{SO}_3\text{H} \), \( \text{SO}_3\text{H} \), \( \text{SO}_3\text{H} \), \( \text{SO}_3\text{H} \) only pendent positions sulfonated in SDAPP polymer

\[ \text{SO}_3\text{H} \text{SO}_3\text{H} \]

**FIG. 23A**

- Reactive groups with pendent positions sulfonated in SDAPP polymer

\[ \text{SO}_3\text{H} \text{SO}_3\text{H} \]

- Reactive groups in FS-SDAPP polymer

\[ \text{SO}_3\text{H} \text{SO}_3\text{H} \]
FIG. 23B
FIG. 23C
FIG. 24
FIG. 25A

FIG. 25B
FIG. 26B

FIG. 26C
FIG. 29

(II-17)

(II-18)
HALO-CONTAINING ANION EXCHANGE MEMBRANES AND METHODS THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of prior application Ser. No. 15/398,545, filed Jan. 4, 2017, now U.S. Pat. No. 10,053,534, issued Aug. 21, 2018, which in turn claims the benefit of U.S. Provisional Application No. 62/274,569, filed Jan. 4, 2016, each of which is hereby incorporated by reference in its entirety.

STATEMENT OF GOVERNMENT INTEREST

This invention was made with Government support under Contract No. DE-NA00003525 awarded by the United States Department of Energy/National Nuclear Security Administration. The Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates to functionalized polymers including a poly(phenylene) structure having modifications suitable for an anion exchange membrane. Exemplary modifications include use of a cationic moiety and a halo moiety. Methods and uses of such structures and polymers are also described herein.

BACKGROUND OF THE INVENTION

Polymers including a poly(phenylene) backbone can provide improved properties, including enhanced chemical stability and/or strength. Thus, such robust polymers have been examined for use in fuel battery cells. However, further use as an anion exchange membrane will require chemical functionalities that impart binding to anionic carriers (e.g., hydroxide or carbonate anions), while maintaining the durability provided by the backbone. Additional starting materials, compositions, and methods to address such concerns are desired.

SUMMARY OF THE INVENTION

The present invention relates to polymer compounds and compositions having a poly(phenylene) structure in combination with a cationic moiety and/or a halo group to impart characteristics beneficial for an anion exchange membrane. For such a membrane, the composition should be capable of binding an anion, e.g., by use of a cationic moiety within the composition. In another instance, the composition should be sufficiently hydrophilic to reduce affinity with water, e.g., by use of a halo group within the composition.

Hydrophilicity can be one non-limiting way to control water affinity of the composition. In some instances, the polymer composition herein can be employed as an anion exchange membrane, which in turn can be employed within a fuel cell. A fuel cell can exhibit poor performance due to flooding, which can occur when the anionic exchange membrane displays high affinity to water. Thus, performance can be improved by employing a sufficiently hydrophobic polymer composition, which also displays binding to an anion carrier.

Accordingly, in one aspect, the present invention features a composition (e.g., a molecule, a monomer, a polymer, an article, etc.) including the formula (I), having the formula (I), or including a structure having the formula (I):

or a salt thereof (e.g., a cationic salt, such as a sodium salt, or a form thereof including a counter ion, such as a hydroxide).

In some embodiments, each and every R_{14}^{14} includes a cationic moiety or a halo. In other embodiments, at least one R_{14}^{14} is R_{14}^{14} (e.g., an aryl, an alkyl, a heteroaryl substituted with the cationic moiety). In yet other embodiments, at least one R_{14}^{14} is R_{14}^{14} (e.g., an aryl, an alkyl, a heteroaryl, or a heteroaryl substituted with the halo). In some embodiments, the cationic moiety includes an anion cation (e.g., any described herein, such as an ammonium cation).

In some embodiments, each R_{14}^{14} includes, independently, optionally substituted alkyl (e.g., C_{1-12} alkyl), optionally substituted haloalkyl (e.g., C_{1-12} haloalkyl), optionally substituted perfluoroalkyl (e.g., C_{1-12} perfluoroalkyl), optionally substituted heteroalkyl (e.g., C_{1-12} heteroalkyl), halo, optionally substituted aryl (e.g., C_{6-18} aryl), optionally substituted aryalkyl (e.g., C_{6-18} alkyl-C_{6-18} aryl), optionally substituted aryalkoxy (e.g., C_{6-18} aryl-C_{12} alkoxy or C_{6-18} arylyl-C_{1-6} alkoxy), optionally substituted arylalkoxy (e.g., C_{6-18} aryloxy, optionally including one or more halo or haloalkyl), optionally substituted aryloxyalkyl (e.g., C_{5-12} aryloxyalkyl), optionally substituted aryl (e.g., C_{2-12} aryl or C_{2-12} aryloxyalkyl), optionally substituted aryloxyalkyl (e.g., C_{6-18} aryloxyalkyl), optionally substituted arylosulfonylalkyl (e.g., C_{6-18} arylsulfonylalkyl), or optionally substituted arylosulfonylalkyl (e.g., C_{6-18} arylsulfonylalkyl).

In some embodiments, each R_{1}^{1} or R_{2}^{1} is, independently, H, halo, optionally substituted C_{1-12} alkyl, optionally substituted C_{1-12} haloalkyl, optionally substituted C_{1-12} perfluoroalkyl, optionally substituted C_{1-12} heteroalkyl, R_{2}^{1}, R_{3}^{1}, R_{4}^{1}, or R_{5}^{1}, where R_{2}^{1} is an acidic moiety including a sulfonate group, R_{3}^{1} is an acidic moiety including a phosphonyl group, R_{4}^{1} is an acidic moiety including a carbonyl group, and R_{5}^{1} is an electron-withdrawing moiety; each Ar_{2}^{1} is, independently, a bivalent linker including optionally substituted arylenes; each Ar_{2}^{1} is, independently, a bivalent linker including optionally substituted arylenes; each q is, independently, an integer of from 0 to 5 (e.g., where each q for R_{2}^{1} is, independently, 0 or 1); each a is, independently, an integer of from 0 to 5, wherein at least one a is not 0; and m is an integer of from 1 to 1000 (e.g., from about 1 to 500).

In further embodiments, at least one R_{1}^{1} or Ar_{2}^{1} in formula (I) includes R_{2}^{1}, R_{3}^{1}, R_{4}^{1}, or R_{5}^{1}. In some embodiments, q for
or a salt thereof (e.g., a cationic salt, such as a sodium salt) or a form thereof including a counter ion (e.g., an anion, such as any described herein). In some embodiments, each of R^{4F} (e.g., R^4 and R^5), R^6, R^3, R^2, Ar^F, Ar^M, q, a, m, n, L, L', and R^L is, independently, any described herein. In some embodiments, each R^L is, independently, an electrophilic reactive end group (e.g., any herein, such as optionally substituted C_{7-11} aryloyl or optionally substituted C_{6-18} aryl). In further embodiments, at least one R^1 or Ar^F or Ar^M in formula (VI) includes R^{4F}, R^4, R^5, R^6, R^3, R^2, Ar^F, or R^L.

or a salt thereof (e.g., a cationic salt, such as a sodium salt) or a form thereof including a counter ion (e.g., an anion, such as any described herein). In some embodiments, each of R^{4F} (e.g., R^4 or R^5), R^1, R^3, Ar^F, Ar^M, q, a, m, n, L, and Ar^* is, independently, any described herein. In some embodiments, each of m and n is, independently, an integer of from about 1 to 1000 (e.g., from about 1 to 500); L is a linking segment; and Ar^* is a hydrophobic segment. In further embodiments, at least one R^1 or Ar^F or Ar^M in formula (VII) includes R^{4F}, R^4, R^5, R^6, R^3, R^2, R^C, or R^L.

In yet another aspect, the present invention features a composition (e.g., a molecule, a monomer, a polymer, an article, etc.) including the formula (VII), having the formula (VIII), or including a structure having the formula (VIII):

or a salt thereof (e.g., a cationic salt, such as a sodium salt) or a form thereof including a counter ion (e.g., an anion, such as any described herein). In some embodiments, each of R^{4F} (e.g., R^4 or R^5), R^1, R^3, R^2, Ar^F, Ar^M, q, a, m, n, L,
In yet another aspect, the present invention features a composition (e.g., a molecule, a monomer, a polymer, an anion and Ar* is, independently, any described herein. In some embodiments, each of m and n is, independently, an integer of from about 1 to 1000 (e.g., from about 1 to 500); L is a linking segment; and Ar* is a hydrophobic segment. In further embodiments, at least one R1' or Ar1' or Ar2' in formula (VII) includes R4F, R4', R5, R7, R7', R5', R5C, or R5E.

In another aspect, the present invention features a composition (e.g., a molecule, a monomer, a polymer, an article, etc.) including the formula (VIIa), having the formula (VIIa), or including a structure having the formula (VIIa):

or a salt thereof (e.g., a cationic salt, such as a sodium salt) or a form thereof including a counter ion (e.g., an anion, such as any described herein). In some embodiments, each of R1F (e.g., R1F or R1'), R1', R1', Ar1', Ar2', q, a, m, n, L, and Ar* is, independently, any described herein. In some embodiments, each of m and n is, independently, an integer of from about 1 to 1000 (e.g., from about 1 to 500); L is a linking segment; and Ar* is a hydrophobic segment. In further embodiments, at least one R1' or Ar1' or Ar2' in formula (VIIa) includes R4F, R4', R5, R7, R7', R5', R5C, or R5E.

In yet another aspect, the present invention features a composition (e.g., a molecule, a monomer, a polymer, an article, etc.) including the formula (IX), having the formula (IX), or including a structure having the formula (IX):

or a salt thereof (e.g., a cationic salt, such as a sodium salt) or a form thereof including a counter ion (e.g., an anion, such as any described herein). In some embodiments, each R1F is, independently, R4F or R5—R5F, where R5F is a functional group including a cationic moiety or a halo, and where R5F is reacted reactive handle (e.g., any herein, where R5F is selected from the group of an optionally substituted alkyl (e.g., C112 alkyl), optionally substituted haloalkyl (e.g., C112 haloalkyl), optionally substituted perfluoroalkyl (e.g., C112 perfluoroalkyl), optionally substituted heteroalkyl (e.g., C112 heteroalkyl), optionally substituted aryalkyl (e.g., C418 aryalkyl), optionally substituted alkenyl (e.g., C112 alk-C418 ary or C418 alko-C418 ary), optionally substituted arylalkoxy (e.g., C418 aryl-C112 alkoxy or C418 aryl-C6 alkoxy), optionally substituted aryloxy (e.g., C418 aryloxy), optionally substituted arylcarbonyl (e.g., C519 aryl-C6-O), optionally substituted aryl-C6-C6-C6-C6 aryl (e.g., C711 aryloxy or C519 aryloxy), optionally substituted arylcarbonylalkyl (e.g., C418 arylcarbonyl-C6-C6-C6-C6 alkyl or C418 aryl-C418 aryloxy), optionally substituted arylsulfonfyl (e.g., C418 arylsulfonfyl), or optionally substituted arylcarbonylalkyl (e.g., C418 aryl-C418 arylsulfonfyl-C6-C6-C6-C6 alkyl)). In some embodiments, each of R4F (e.g., R4F or R5'), R1, R1', Ar1', Ar2', q, h*m, and m is, independently, any described herein. In some embodiments, each h*m is, independently, an integer of from 0 to 5, wherein at least one h*m is not 0. In further embodiments, at least one R1' or Ar1' or Ar2' in formula (IX) includes R4F, R4', R5, R7, R7', R5', R5C, or R5E.
In some embodiments, the first composition is present in a polymeric membrane.

In any embodiment herein, L or L' includes a covalent bond, optionally substituted C1-12 alkylene, optionally substituted C1-12 alkyleneoxy, optionally substituted C1-12 heteroalkylene, optionally substituted C1-12 heteroalkyleneoxy, optionally substituted C4-18 arylene, optionally substituted C4-18 aryleneoxy, optionally substituted polyphenylene, or a structure of formula (II). In yet other embodiments, L or L' includes a structure of formula (I) and Ar*(e.g., any subunits described herein for Ar*).

In any embodiment herein, Ar* or L or L' includes a structure of formula (I), a sulfone subunit, an arylene sulfone subunit, an ether sulfone subunit, an arylene ether subunit, a perfluoroalkyl subunit, or a perfluoroalkoxy subunit.

In any embodiment herein, each of Ar2, Ar4, and Ar* is optionally substituted phenylene, optionally substituted naphthylene, optionally substituted phenanthrylene, a sulfone subunit, an arylene sulfone subunit, an ether sulfone subunit, an arylene ether subunit, a perfluoroalkyl subunit, a perfluoroalkoxy subunit, or any described herein (e.g., any aryl group described herein). In further embodiments, the optional substitution is R1, R2, R3, R4, R5, R6, R7, or a label (e.g., fluorine or another NMR detectable label).

In any embodiment herein, m is less than n. In any embodiment herein, m is more than n.

In any embodiment herein, the cationic moiety includes an onium cation (e.g., an ammonium cation, a sulfonium cation, a phosphonium cation, an oxonium cation, a diazonium cation, or a halonium cation).

In any embodiment herein, the counter ion is an anion (e.g., a hydroxide anion (OH-), a halide anion (e.g., a chloride anion, a bromide anion, or a fluoride anion), or any described herein).

In any embodiment herein, R is a reactive handle. In some embodiments, each R is, independently, H, optionally substituted alkyl (e.g., C1-12 alkyl), optionally substituted haloalkyl (e.g., C1-12 haloalkyl), optionally substituted perfluoroalkyl (e.g., C1-12 perfluoroalkyl), optionally substituted heteroalkyl (e.g., C1-12 heteroalkyl), halo, optionally substituted aryl (e.g., C4-18 aryl), optionally substituted alkaryl (e.g., C1-12 alk-C4-18 aryl or C1-6 alk-C4-18 aryl), optionally substituted arylalkoxy (e.g., C4-18 aryl-C1-12 alkoxy or C4-18 aryl-C1-6 alkoxy), optionally substituted aryl oxy (e.g., C4-18 arylox or C4-18 arylox), optionally substituted aryl oxycarboxyl (e.g., C5-15 aryloxycarboxyl), optionally substituted arlyloxoy (e.g., C7-15 arlyloxoy), optionally substituted arlyloxycarboxyl (e.g., C5-15 arlyloxycarboxyl), optionally substituted aryloxoy (e.g., C4-18 arylox), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxycarboxyl (e.g., C5-15 aryloxycarboxyl), optionally substituted aryloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), optionally substituted aryloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), optionally substituted arlyloxoy (e.g., C4-18 aryloxoy), or optionally substituted arlyloxoy (e.g., C4-18 aryloxoy). In other embodiments, R is -R2-ArH or R is -L2-AkH (e.g., ArH is an optionally substituted aryl (e.g., substituted with one or more substitutions selected from the group of halo, cyano, optionally substituted haloalkyl, optionally substituted perfluoroalkyl, optionally substituted nitroalkyl, and optionally substituted alkyl); AkH is an optionally substituted alkyl or optionally substituted heteroalkyl (e.g., substituted with one or more substitutions selected from the group of halo, cyano, optionally substituted haloalkyl, optionally substituted perfluoroalkyl, optionally substituted nitroalkyl, and optionally substituted alkyl); and L is a linker, such as any described herein for L').

In any embodiment herein, R is R4, R4, or R5; and h can be a.

In any embodiment herein, R is R4 or R4. In any embodiment herein, R can be reacted with a reactant to provide an R4, R4, or R5 group.

In any embodiment herein, R can be reacted with a reactant to provide R4 or R5.

Definitions

As used herein, the term “about” means +/-10% of any recited value. As used herein, this term modifies any recited value, range of values, or endpoints of one or more ranges.

The term “acyl,” or “alkanoyl,” as used interchangeably herein, represent an alkyl group, as defined herein, or hydrogen attached to the parent molecular group through a carbonyl group, as defined herein. This group is exemplified by formyl, acetyl, propionyl, butanoyl, and the like. The alkanoyl group can be substituted or unsubstituted. For example, the alkanoyl group can be substituted with one or more substitution groups, as described herein for alkyl. In some embodiments, the unsubstituted acyl group is a C2-7 acyl or alkanoyl group.

By “alkyl” is meant an aryl group, as defined herein, attached to the parent molecular group through an alkylene group, as defined herein. Similarly, by the term “alketryl” is meant a heteroaryl group, as defined herein, attached to the parent molecular group through an alkylene group. Other groups preceded by the prefix “alk-” are defined in the same manner. The alkylene group can be substituted or unsubstituted. For example, the alkylene group can be substituted with one or more substitution groups, as described herein for alkyl and/or aryl. Exemplary unsubstituted alkylene groups are of from 2 to 16 carbons (C2-16 alkylene), as well as those having an alkylene group with 1 to 6 carbons and an arylene group with 4 to 18 carbons (i.e., C1-6 alk-C4-18 aryl).

By “alkycycloalkyl” is meant a cycloalkyl group, as defined herein, attached to the parent molecular group through an alkylene group, as defined herein. The cycloalkyl group can be substituted or unsubstituted. For example, the alkycycloalkyl group can be substituted with one or more substitution groups, as described herein for alkyl.

By “alkenyl” is meant an optionally substituted C2-24 alkyl group having one or more double bonds. The alkenyl group can be cyclic (e.g., C3-24 cycloalkenyl) or acyclic. The alkenyl group can also be substituted or unsubstituted. For example, the alkenyl group can be substituted with one or more substitution groups, as described herein for alkyl.

By “alkynyl” is meant a heterocyclyl group, as defined herein, attached to the parent molecular group through an alkylene group, as defined herein. Exemplary unsubstituted alkynyl groups are of from 2 to 14 carbons.

By “alkoxy” is meant —OR, where R is an optionally substituted alkyl group, as described herein. Exemplary alkoxy groups include methoxy, ethoxy, butoxy, trialkylalkoxy, such as trifluoromethoxy, etc. The alkoxy group can be substituted or unsubstituted. For example, the alkoxy group can be substituted with one or more substitution groups, as described herein for alkyl. Exemplary unsubstituted alkoxyalkyl groups include C1-3, C1-6, C1-12, C1-16, C1-18, C1-20, or C1-24 alkoxy groups.

By “alkoxyalkyl” is meant an alkyl group, as defined herein, which is substituted with an alkoxy group, as defined herein. Exemplary unsubstituted alkoxyalkyl groups include between 2 to 12 carbons (C2-12 alkoxyalkyl), as well as those having an alkyl group with 1 to 6 carbons and an alkoxy group with 1 to 6 carbons (i.e., C1-6 alk-C1-6 alkoxy).
By “alkoxy carbonyl” is meant an alkoxy group, as defined herein, that is attached to the parent molecular group through a carbonyl group. In some embodiments, the unsubstituted alkoxy carbonyl group is a \( C_{1-6} \) alkoxy carbonyl group.

By “alkyl” and the prefix “alk” is meant a branched or unbranched saturated hydrocarbon group of 1 to 24 carbons, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, t-butyl, n-pentyl, isopentyl, s-pentyl, neo-pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, eicosyl, tetracosyl, and the like. The alkyl group can be cyclic (e.g., \( C_{3-4} \) cycloalkyl) or acyclic. The alkyl group can also be substituted or unsubstituted. For example, the alkyl group can be substituted with one, two, three or, in the case of alkyl groups of two carbons or more, four substituents independently selected from the group consisting of: (1) \( C_{1-6} \) alkyl; (2) \( C_{1-6} \) alkoxy; (3) \( C_{1-6} \) alkyloxy; (4) aminos; (5) ary; (6) aralkyloxy; (7) aryloxy; (8) azido; (9) cyano; (10) carbonic/hydroxy; (11) \( C_{1-6} \) cycloalkyl; (12) halo; (13) heterocyclic; (14) heterocyclyl; (15) heterocyclyl; (16) hydroxy; (17) N-protected amino; (18) nitro; (19) oxo; (20) \( C_{1-6} \) spirocycyl; (21) \( C_{1-6} \) thiol; (22) thiol; (23) \( CO_{4} \), where \( R^{4} \) is selected from the group consisting of: (a) hydrogen, (b) \( C_{1-6} \) alkyl, (c) \( C_{1-6} \) ary, and (d) \( C_{1-6} \) alk-C=18 ary; (24) \( C=O \)NR\( R^{2} \), where each of \( R^{2} \) and \( R^{2} \) is, independently, selected from the group consisting of: (a) hydrogen, (b) \( C_{1-6} \) alkyl, (c) \( C_{1-6} \) ary, and (d) \( C_{1-6} \) alk-C=18 ary; (25) \( SO_{2} \), where \( R^{2} \) is selected from the group consisting of: (a) \( C_{1-6} \) alkyl, (b) \( C_{1-6} \) ary, and (c) \( C_{1-6} \) alk-C=18 ary; (26) \( SO_{2} \)NR\( R^{2} \), where each of \( R^{2} \) is, independently, selected from the group consisting of: (a) hydrogen, (b) \( C_{1-6} \) alkyl, (c) \( C_{1-6} \) ary, and (d) \( C_{1-6} \) alk-C=18 ary; (27) \( NR_{2} \), where each of \( R^{2} \) and \( R^{2} \) is, independently, selected from the group consisting of: (a) hydrogen, (b) an N-protecting group, (c) \( C_{1-6} \) alkyl, (d) \( C_{1-6} \) alkenyl, (e) \( C_{1-6} \) alkenyl, (f) \( C_{1-6} \) ary, (g) \( C_{1-6} \) alk-C=18 ary, (h) \( C_{1-6} \) cycloalkyl, and (i) \( C_{1-6} \) alk-C=3 cycloalkyl, wherein in one embodiment no two groups are bound to the nitrogen atom through a carbonyl group or a sulfonyl group. The alkyl group can be a primary, secondary, or tertiary alkyl group substituted with one or more substituents (e.g., one or more halo or alkoxy). In some embodiments, the unsubstituted alkyl group is a \( C_{1-3} \), \( C_{1-6} \), \( C_{1-12} \), \( C_{1-16} \), \( C_{1-20} \), or \( C_{1-24} \) alkyl group.

By “aldehyde” is meant a bivalent form of an alkyl group, as described herein. Exemplary aldehyde groups include methylene, ethylene, propylene, butylene, etc. In some embodiments, the aldehyde group is a \( C_{1-6} \), \( C_{1-6} \), \( C_{1-12} \), \( C_{1-10} \), \( C_{1-20} \), \( C_{2-22} \), \( C_{2-20} \), \( C_{2-22} \), \( C_{2-16} \), \( C_{2-8} \), \( C_{2-20} \) or \( C_{2-24} \) aldehyde group. The alkyl group can be branched or unbranched. The alkyl group can also be substituted or unsubstituted. For example, the alkylene group can be substituted with one or more substitution groups, as described herein for alkyl.

By “aldehydeoxy” is meant an alkyl group, as defined herein, attached to the parent molecular group through an oxygen atom. By “alkyl sulfonate” is meant an alkyl group, as defined herein, attached to the parent molecular group through an \( =\text{O}-\text{SO}_{3} \)- group. An exemplary alkyl sulfonate group is \( =\text{O}-\text{SO}_{3} \)-Ak, where each Ak is, independently, optionally substituted alkyl.

By “alkyl sulfanyl” is meant an alkyl group, as defined herein, attached to the parent molecular group through an alkyl sulfanyl group. In some embodiments, the unsubstituted alkyl sulfanyl group is a \( C_{1-6} \) or \( C_{1-12} \) alkyl sulfanyl group.
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CT, Br, or I), a hydroxide (e.g., OH−), a borate (e.g., tetrafluoroborate (BF4−)), a carbonate (e.g., CO32− or HCO3−), or a sulfate (e.g., SO42−).

By “aryl” is meant a group that contains any carbon-based aromatic group including, but not limited to, benzyl, naphthalene, phenyl, biphenyl, phenoxycene, and the like. The term “aryl” also includes “hetaryl,” which is defined as a group that contains an aromatic group that has at least one heterocent incorporated within the ring of the aromatic group. Examples of hetaromatics include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. Likewise, the term “non-heteroaryl,” which is also included in the term “aryl,” defines a group that contains an aromatic group that does not contain a heterocent. The aryl group can be substituted or unsubstituted. The aryl group can be substituted with one, two, three, four, or five substituents independently selected from the group consisting of: (1) C1−6 alkanyl; (2) C1−6 alkyll; (3) C1−6 alkoxy; (4) C1−6 alkoxy-C1−6 alkyl; (5) C1−6 alkylsulfonyl; (6) C1−6 alkylsulfonyl-C1−6 alkyl; (7) C1−6 alkylsulfonyl-8; (8) C1−6 alkylsulfonyl-C1−6 alkyl (9) C1−6 amino; (10) C1−6 alkoxyamino; (11) C1−6 aryl; (12) C1−6 alk-C1−6 aryl; (13) C1−6 alk-C1−6 alkyl; (14) C1−6 aryl; (15) azido; (16) cyan; (17) C1−6 azido; (18) carboxyalkyloxy; (19) carboxyalkylamide-C1−6 alkyl; (20) C1−6 carboxyalkyl; (21) C1−6 alk-C1−6 carboxyalkyl; (22) halo; (23) C1−6 haloalkyl; (24) heterocenyl; (25) heterocyclyloxy; (26) heterocyclyl; (27) hydroxy; (28) C1−6 hydroxyalkyl; (29) nitro; (30) C1−6 nitroalkyl; (31) N-protected amino; (32) N-protected amino-C1−6 alkyl; (33) oxo; (34) C1−6 thioalkoxy; (35) thioc1−6 alkyl-C1−6 alkyl; (36) (CH2)nCO2R, where n is an integer from zero to four, and R is selected from the group consisting of: (a) hydroxy, (b) C1−6 alkyl, (c) C1−6 aryl, and (d) ary1 (37) —(CH2)n(CONR)R, where n is an integer from zero to four and where each R and R1 is independently selected from the group consisting of: (a) hydroxy, (b) C1−6 alkyl, (c) C1−6 aryl, and (d) C1−6 alk-C1−6 aryl; (38) —(CH2)nSO2R, where n is an integer from zero to four and where R is selected from the group consisting of: (a) C1−6 alkyl, (b) C4−18 aryl, and (c) C1−6 alk-C4−18 aryl; (39) —(CH2)nSO2NR2R2, where n is an integer from zero to four and where each of R and R1 is independently selected from the group consisting of: (a) hydrogen, (b) C1−6 alkyl, (c) C1−6 aryl, and (d) C1−6 alk-C1−6 aryl; (40) —(CH2)nNR2R2, where n is an integer from zero to four and where each of R and R1 is independently selected from the group consisting of: (a) hydrogen, (b) an N-protecting group, (c) C1−6 alkyl, (d) C4−18 aryl, (e) C1−6 alk-C4−18 aryl, (f) C4−18 aryl, (g) C1−6 alk-C4−18 aryl, (h) C2−6 cycloalkyl, and (i) C1−6 alk-C2−6 cycloalkyl, wherein in one embodiment no two groups are bound to the nitrogen atom through a carbonyl group or a sulfonyl group; (41) thiol; (42) perfluorocarbon; (43) perfluoroalkoxy; (44) aryloxy; (45) cycloalkyloxy; (46) cycloalkylalkoxy; and (47) arylalkoxy. In particular embodiments, an unsubstituted aryl group is a C6−12 alkyl-C6−12 alkyl, C6−12 alkyl-C1−6 aryl, or C6−12 aryl group.

By “arylcarbonylalkyl” is meant an alkyl group, as defined herein, substituted by an arylcarbonyl group, as defined herein. In some embodiments, the arylcarbonylalkyl group is Ar—C(O)—R, in which Ar is an optionally substituted aryl group and R is an optionally substituted alkyl or optionally substituted alkenyl group. In particular embodiments, an unsubstituted arylcarbonylalkyl group is a C3−4 alkyl-C(O)—C1−12 alkyl group or a C4−12 aryl-C(O)—C1−12 alkyl group.

By “aryl” is meant a bivalent form of an aryl group, as described herein. Exemplary aryl groups include phenyl, naphthyl, biphenyl, triphenyl, diphenyl ether, anenaphenylgly, anthylene, or phenanthrylene. In some embodiments, the aryl group is a C9−18 alkyl-C9−18 alkyl, C9−18 alkyl-C12−18 alkyl, C9−18 aryl-C12−18 alkyl, or C9−18 aryl group. The aryl group can be branched or unbranched. The aryl group can also be substituted or unsubstituted. For example, the aryl group can be substituted with one or more substitution groups, as described herein for aryl.

By “arylalkoxy” is meant an alkyl group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “arylalkyl” is meant an alkyl group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “aryloxy” is meant —OR, where R is an optionally substituted aryl group, as defined herein. In some embodiments, an unsubstituted aryloxy group is a C6−18 or C6−18 arylalkoxy group.

By “aryloxy carbonyl” is meant an aryloxy group, as defined herein, that is attached to the parent molecular group through a carbonyl group. In some embodiments, an unsubstituted aryloxy carbonyl group is a C6−18 or C6−18 aryloxy carbonyl group.

By “aryloxy” is meant an aryl group that is attached to the parent molecular group through a carbonyl group. In some embodiments, an unsubstituted aryloxy group is a C7−11 aryl or C6−18 aryl group.

By “arylsulfonyl” is meant an aryl group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “arylsulfonylalkyl” is meant an alkyl group, as defined herein, substituted by an arylsulfonyl group. In some embodiments, the arylsulfonylalkyl group is Ar—SO2—C1−2 alkyl, in which Ar is an optionally substituted aryl group and R is an optionally substituted alkyl or optionally substituted alkenyl group. In particular embodiments, the unsubstituted arylsulfonylalkyl group is a C4−18 ary1—SO2—C1−2 alkyl group or a C4−18 ary1—SO2—C1−2 alkyl group.

By “azido” is meant an —N3group.

By “azo” is meant an —N=N— group.

By “azidoalkyl” is meant an azido group attached to the parent molecular group through an alkyl group, as defined herein.

By “carbonyl” is meant a —C(O)— group, which can also be represented as —C=O.

By “carboxyalkyloxy” is meant a —C(O)R group.

By “carboxyalkyloxy” is meant a carboxyalkyloxy group, as defined herein, attached to the parent molecular group through an alkene group, as defined herein.

By “carboxy” is meant a —CO2H group.

By “cyan” is meant an CN group.

By “cycloalkyl” is meant a monocyclic saturated or unsaturated non- aromatic cyclic hydrocarbon group of from three to eight carbons, unless otherwise specified, and is exemplified by cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cicloheptyl, bicyclo[2.2.1]heptyl and the like. The cycloalkyl group can also be substituted or unsubstituted. For example, the cycloalkyl group can be substituted with one or more groups including those described herein for alkyl.

By “cycloalkoxy” is meant a cycloalkyloxy group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “diazonium” is meant a group including —N=N+.

By “dithiocarbamino” is meant —NR[1]C(S)SR[2], where each of R[1] and R[2] is, independently, H or optionally
substituted alkyl, or R″¹ and R″¹, taken together with the nitrogen atom to which each are attached, form a heterocyclic group, as defined herein.

By “halo” is meant F, Cl, Br, or I.

By “haloalkyl” is meant an alkyl group, as defined herein, substituted with one or more halo.

By “halonium” is meant a group including —X−, where X is halo as defined herein. Exemplary halonium groups include an iodonium group (e.g., —I−), a bromonium group (e.g., —Br−), a chloronium group (e.g., —Cl−), or a fluoronium group (e.g., —F−).

By “heteroalkyl” is meant an alkyl group, as defined herein, containing one, two, three, or four non-carbon heteroatoms (e.g., independently selected from the group consisting of nitrogen, oxygen, phosphorus, sulfur, or halo).

By “heteroalkylene” is meant a divalent form of an alkylene group, as defined herein, containing one, two, three, or four non-carbon heteroatoms (e.g., independently selected from the group consisting of nitrogen, oxygen, phosphorus, sulfur, or halo).

By “heteroalkyleneoxy” is meant a heteroalkylene group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “heteroary” is meant a subset of heterocyclic groups, as defined herein, which are aromatic, i.e., they contain 4n+2 pi electrons within the mono- or multicyclic ring system.

By “heterocyclic” is meant a 5-, 6- or 7-membered ring, unless otherwise specified, containing one, two, three, or four non-carbon heteroatoms (e.g., independently selected from the group consisting of nitrogen, oxygen, phosphorus, sulfur, or halo). The 5-membered ring has zero to two double bonds and the 6- and 7-membered rings have zero to three double bonds. The term “heterocyclic” also includes bicyclic, tricyclic and tetracyclic groups in which any of the above heterocyclic rings is fused to one, two, or three rings independently selected from the group consisting of an aryl ring, a cyclohexane ring, a cyclopentene ring, and another monocyclic heterocyclic ring, such as indolyl, quinolyl, isoquinolyl, tetrahydroquinolinyl, benzofuryl, benzothienyl and the like. Heterocyclics include thiiranyl, thietanyl, tetrahydrothienyl, thianyl, thiophenyl, azidinyl, azetidinyl, pyrrolidinyl, piperidinyl, azepanyl, pyrrolyl, pyrrolidinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, imidazolyl, imidazolinyl, imidazolidinyl, pyridyl, homopiperidinyl, pyrazinyl, pyperazinyl, pyrimidinyl, pyridazinyl, oxazolyl, oxazolinyl, isoxazolyl, isoxazolidinyl, morpholinyl, thiomorpholinyl, thiazolyl, thiazolinyl, isoaxazolyl, isothiazolyl, indolyl, quinolinyl, isoquinolinyl, benzimidazolyl, benzothiazolyl, benzoxazolyl, furyl, thienyl, thiophenyl, isothiazolyl, isoindolyl, triazolyl, tetrazolyl, oxadiazolyl, uracil, thiadiazolyl, pyrimidyl, tetrahydrofuranyl, dihydrofuranyl, tetrahydrothienyl, dihydrothienyl, dihydroindolyl, tetrahydroquinolinyl, tetrahydroisoquinolinyl, pyranyl, dihydropropyl, thiadiazolyl, benzofuranyl, benzothienyl, and the like.

By “heteroarylcycloxy” is meant a heterocyclic group, as defined herein, attached to the parent molecular group through an oxygen atom.

By “heteroarylcycloxy” is meant a heterocyclic group, as defined herein, attached to the parent molecular group through a carbonyl group.

By “hydroxy” is meant —OH.

By “hydroxalkyl” is meant an alkyl group, as defined herein, substituted by one to three hydroxy groups, with the proviso that no more than one hydroxy group may be attached to a single carbon atom of the alkyl group and is exemplified by hydroxymethyl, dihydroxypropyl, and the like.

By “imine” is meant —CR=NR1−, where R=H or optionally substituted alkyl.

By “iminooxy” is meant —HN−.

By “nitrilo” is meant —NO−. Exemplary nitrilo groups include —NR2−3, where R2−3 is H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted alkoxy, optionally substituted alkoyl, optionally substituted aryl, or halo.

By “nitro” is meant an —NO2 group.

By “nitroalkyl” is meant an alkyl group, as defined herein, substituted by one to three nitro groups.

By “nitroso” is meant an —NO group.

By “oxo” is meant an —O group.

By “oxonium” is meant a group including a protonated oxygen atom O+. Exemplary oxonium groups include —O−R=2R=2, where each of R=2 and R=2 is, independently, H, optionally substituted alkyl, optionally substituted aryl, or optionally substituted alkoxy, or wherein R=2 and R=2, taken together, form an optionally substituted alkylene or heteroalkylene (e.g., as described herein).

By “oxy” is meant —O−.

By “perfluoroalkyl” is meant an alkyl group, as defined herein, having each hydrogen atom substituted with a fluorne atom. Exemplary perfluoroalkyl groups include trifluoromethyl, pentfluoroethyl, etc.

By “perfluoroalkylene” is meant an alkylene group, as defined herein, having each hydrogen atom substituted with a fluorne atom. Exemplary perfluoroalkylene groups include difluoromethylene, tetrafluoroethylenyl, etc.

By “perfluoroalkyleneoxy” is meant a perfluoroalkylene group, as defined herein, having an oxy group attached to either end of the perfluoroalkylene group. Exemplary perfluoroalkylene groups include, e.g., —OCF=2— or —CF=2O—, where f is an integer from about 1 to 5, and 2f is an integer that is 2 times f (e.g., difluoromethoxyene, tetrafluoroethylenoxy, etc.).

By “perfluoroalkoxy” is meant an alkyl group, as defined herein, having each hydrogen atom substituted with a fluorne atom.

By “phosphine” is meant a —PR=2— group, where R=2 is H or optionally substituted alkyl.

By “phosphonium” is meant a group including a protonated phosphorous atom P=+. Exemplary phosphonium groups include —P=RR=2RR=2, where each of R=2 and R=2 is, independently, H, optionally substituted alkyl, optionally substituted aryl, or optionally substituted alkoyl; or wherein two of R=2, R=2, and R=2, taken together, form an optionally substituted alkylene or heteroalkylene (e.g., as described herein).

By “phosphono” is meant a —PO(OH)= group.

By “phosphonyl” is meant a —PO(OH)— group.

By “phosphoric ester” is meant a —O−PO(OH)= group.

By “phosphonyl” is meant a —PO=h-group.

By “protecting group” is meant any group intended to protect a reactive group against undesirable synthetic reactions. Commonly used protecting groups are disclosed in “Greene’s Protective Groups in Organic Synthesis,” John Wiley & Sons, New York, 2007 (4th ed., eds. P. G. M. Wuts and T. W. Greene), which is incorporated herein by reference. O-protecting groups include an optionally substituted alkyl group (e.g., forming an ether with reactive group O), such as methyl, methoxymethyl, methylthiomethyl, benzoxymethyl, t-butoxymethyl, etc.; an optionally substituted
alkanoyl group (e.g., forming an ester with the reactive group O), such as formyl, acetyl, chloroacetyl, fluoroacetyl (e.g., perfluoroacetyl), methoxyacetyl, pivaloyl, t-buty lacetyl, phenoxyacetyl, etc.; an optionally substituted aryl group (e.g., forming an ester with the reactive group O), such as −C(O)−Ar, including benzoyl; an optionally substituted alkylsulfonyl group (e.g., forming an alkylsulfonyl with reactive group O), such as −SO₂−R², where R² is optionally substituted C₄₋₁₅ alkyl, such as mesyl or benzyl sulfonyl, an optionally substituted arylsulfonyl group (e.g., forming an arylsulfonyl with reactive group O), such as −SO₂−R⁴, where R⁴ is optionally substituted C₄₋₁₅ aryl, such as tosyl or phenylsulfonyl; an optionally substituted alkoxyacarbonyl or aryl oxycarbonyl group (e.g., forming a carbonate with reactive group O), such as −C(O)−OR³, where R³ is optionally substituted C₁₋₁₂ alkyl or optionally substituted t-Bu₄₋₁₈ aryl, such as methoxyacarbonyl, methoxymethylcarbonyl, t-butyloxycarbonyl (Boc), or benzoxycarbonyl (Cbz); or an optionally substituted silyl group (e.g., forming a silyl ether with reactive group O), such as −Si−(R²)₃₂, where each R² is, independently, optionally substituted C₁₋₁₂ alkyl or optionally substituted C₁₋₁₂ aryl, such as trimethylsilyl, t-butyldimethylsilyl, or t-butyldiphenylsilyl. N-protecting groups include, e.g., formyl, acetyl, benzoyl, pivaloyl, t-butyloxycarbonyl, alanyl, phenylsulfonyl, benzyl, Boc, and Cbz. Such protecting groups can employ any useful agent to cleave the protecting group, thereby restoring the reactivity of the unprotected reactive group.

By “salt” is meant an ionic form of a compound or structure (e.g., any formulas, compounds, or compositions described herein), which includes a cation or anion compound to form an electrically neutral compound or structure. Salts are well known in the art. For example, non-toxic salts are described in Berge S M et al., “Pharmaceutical Salts.” J. Pharm. Sci. 1977 January; 66(1):1-9; and in “Handbook of Pharmaceutical Salts: Properties, Selection, and Use,” Wiley-VCH, April 2011 (2nd rev. ed., eds. P. H. Stahl and C. G. Wermuth). The salts can be prepared in situ during the final isolation and purification of the compounds of the invention or separately by reacting the free base group with a suitable organic acid (thereby producing an anionic salt) or by reacting the acid group with a suitable metal or organic salt (thereby producing a cationic salt). Representative anionic salts include acetate, adipate, alginate, ascorbate, aspartate, benzenesulfonate, benzoate, bicarbonate, bisulfate, bitartrate, borate, bromide, butyrate, camphorate, camphorsulfonate, chloride, citrate, cyclopentanepropionate, dglucuronate, dihydrocholate, diphosphate, dodecylsulfate, edetate, ethanesulfonate, fumarate, gluconate, heptanoate, hexanoate, hydrobromide, hydrochloride, hydroiodide, hydroxyethanesulfonate, hydroxymyristate, iodide, lactate, lactobionate, lactate, lauryl sulfate, maleate, maleate, malonate, mandelate, mesylate, methanesulfonate, methyl bromide, methyl nitrate, methyl sulfate, mucate, 2-naphthalenesulfonate, nicotinate, nitrate, oleate, oxalate, palmitate, pamoate, pectinate, persulfate, 3-phenylpropionate, phosphate, picate, pivalate, polyglacturonate, propionate, salicylate, searate, subacetate, succinate, sulfate, tartrate, theophyllinate, thiocyanate, triethylde, toluene sulfonate, undecanote, valerate salts, and the like. Representative cationic salts include metal salts, such as alkali or alkaline earth salts, e.g., barium, calcium (e.g., calcium edetate), lithium, magnesium, potassium, sodium, and the like; other metal salts, such as aluminum, bismuth, iron, and zinc; as well as non-toxic ammonium, quaternary ammonium, and amine cations, including, but not limited to ammonium, tetramethylammonium, tetraethylammonium, methylamine, dimethylamine, trimethylamine, triethylamine, ethylamine, pyridinium, and the like. Other cationic salts include organic salts, such as chloropropanec, choline, dibenzylmethylammonium, diethanolammonium, ethylenediamine, methylglycine, and propraine. Yet other salts include ammonium, sulfoxonium, phosphonium, imini mum, imidazolium, benzimidazolium, amidinium, guanidinium, phosphazinium, phosphazene, pyridinium, etc., as well as other cationic groups described herein (e.g., optionally substituted isoxazolium, optionally substituted triazolium, optionally substituted pyrrolium, optionally substituted uraninium, optionally substituted thionanium, optionally substituted imidazolium, optionally substituted pyrazolium, optionally substituted isothiazolium, optionally substituted triazolium, optionally substituted tetrazolium, optionally substituted pyridazinium, optionally substituted pyrrolidinium, optionally substituted furazanum, optionally substituted pyridinium, optionally substituted pyrazinium, optionally substituted triazinium, optionally substituted tetrazinium, optionally substituted pyridazinium, optionally substituted oxazinium, optionally substituted pyrrolidinium, optionally substituted pyrazolium, optionally substituted imidazolium, optionally substituted isoxazolium, optionally substituted oxazolidinium, optionally substituted isoxazolinium, optionally substituted isoxazolidinum, and optionally substituted purinun).

By “spirocyclyl” is meant an alkylene diradical, both ends of which are bonded to the same carbon atom of the parent group to form a spirocyclyl group and also a heteroalkylene diradical both ends of which are bonded to the same atom. By “sulfonyl” is meant an −SO₂− group. By “sulfo” is meant an −SO⁻ group. By “sulfinyl” is meant an −SO(O)− group. By “sulfide” is meant an −SR− group. By “sulfone” is meant R−SO₂−R’. By “sulfur” is meant an −SR− group. By “sulfoneamide” is meant an RN⁺S(O)− or an −SR−S(O)− group, in which R⁻ is any useful moiety. Exemplary R⁻ groups include H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted alkyl, optionally substituted aryl, or halo.

By “sulfonyl” is meant an −SO₂− group. By “sulfonamide” is meant an −SO₂− or an −SR− group. By “sulfonium” is meant a protonated sulfur atom S⁺. Exemplary sulfonium groups include
halo group) and L\(^{-}\) (i.e., a linker, such as any herein). Provided are structures (A) having formulas (1-5) to (1-6); and (B) having formulas (1-7) to (1-8).

FIG. 6A-6B shows schematics of exemplary polymer structures, including (A) an exemplary polymer for an anion exchange membrane and (B) an exemplary poly(arylene ether) polymer for another anion exchange membrane.

FIG. 7A-7B shows graphs of mechanical strength testing of (A) an anion exchange membrane including the polymer in FIGS. 6A and (B) an anion exchange membrane including the polymer in FIG. 6B. In FIG. 7A, provided are data for (i) control (Br\(^{-}\) ions); (ii) treatment with 0.5M NaOH for 1 hour at 80º C. (OH\(^{-}\) ions); (iii) treatment with NaOH, then 0.5M HBr for 1 hour at 25º C. (Br\(^{-}\) ions); and (iv) treatment with NaOH, then HBr, and then NaOH (OH\(^{-}\) ions). In FIG. 7B, provided are data for (i) control; (ii) treatment with 0.01M NaOH for 1 hour at room temperature; (iii) treatment with 0.5M NaOH for 30 minutes at room temperature; and (iv) treatment with 0.5M NaOH for 30 minutes at 80º C.

FIG. 8 shows an exemplary reaction scheme to provide the polymer structure of formula (Ih). Provided is a reaction scheme for reacting an initial polymer (III) in the presence of a reagent (e.g., R\(^{29}\)-X) to form a reactive polymer (I(a)) having three reactive handles R\(^{29}\) appended to three pendant aryl groups. Then, reactive polymer (I(a)) is treated with a further reagent (e.g., R\(^{27}\)-X) to form a further reactive polymer (I(b)) having three other reactive handles R\(^{27}\) appended to three other pendant aryl groups. Finally, polymer (I(b)) is treated with a reagent (e.g., R\(^{25}\)) to form a resultant polymer (Ih) having cationic moieties (R\(^{24}\)) and halo groups (R\(^{26}\), when R\(^{25}\) is chosen to be a chemical moiety having a halo group). In this non-limiting manner, orthogonal chemistries can be installed on the same polymer structure.

FIG. 9A-9C shows schematics of exemplary reaction schemes to provide polymer structures with one or more substituents including a cationic moiety (R\(^{2}\)) or a halo group (R\(^{21}\)). Provided is (A) an exemplary reaction of a labeled Diehl-Alder poly(phenylene) polymer (labeled “F-labeled DAPP") in the presence of a reagent (e.g., R\(^{27}\)-X, such as R\(^{23}\)-Ar–C(O)–X) to form a DAPP (IV-1) having three R\(^{28}\) substituents appended on three pendant aryl groups of the DAPP (e.g., in which R\(^{28}\) is –C(O)–Ar–R\(^{27}\)). Then, DAPP polymer (IV-1) is reacted with a second reagent (e.g., R\(^{22\prime}\)-X, such as R\(^{21}\)-Ar–C(O)–X) to form hydrophobic DAPP (IV-2) having three R\(^{21}\) substituents appended on three other pendant aryl groups of the DAPP (e.g., in which R\(^{21}\) is –C(O)–Ar–R\(^{22\prime}\)). Also provided is (B) a reaction to form a cationic, hydrophobic film using polymer (IV-2), which was provided as a cast film and then reacted in the presence of a reagent (e.g., R\(^{21}\)) to provide polymer (IV-3) including cationic moieties (e.g., R\(^{21}\) that is –C(O)–Ar–R\(^{29}\), in which R\(^{29}\) is an anion) and halo groups (e.g., R\(^{26}\) that is –C(O)–Ar–R\(^{27}\)), in which R\(^{27}\) is halo). Alternatively, the reaction includes forming a cationic moiety and then casting the polymer, as shown in (C), in which polymer (IV-2) is reacted in the presence of a reagent (e.g., R\(^{21}\)) to provide polymer (IV-3) including cationic moieties (e.g., R\(^{21}\) that is –C(O)–Ar–R\(^{29}\), in which R\(^{29}\) is an anion) and halo groups (e.g., R\(^{26}\) that is –C(O)–Ar–R\(^{27}\)), in which R\(^{27}\) is halo). Then, polymer (IV-3) is cast as film. In any embodiment herein, the anion is R\(^{28}\). Alternatively, an anion exchange reaction can be conducted, thereby swapping R\(^{29}\) for any other useful anion (e.g., any described herein).

FIG. 10 shows a schematic of an exemplary reaction scheme to provide polymer structure (IV-5). Provided is an exemplary reaction of a hydrophobic DAPP (IV-2) having

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 shows a schematic of an exemplary polymer structure having one or more functional groups including a cationic moiety and/or a halo group (R\(^{2}\)).

FIG. 2A-2C shows schematics of exemplary polymer structures having an aryl group including a cationic moiety and/or a halo group (R\(^{2}\)) or an aryl group including a cationic moiety and/or a halo group (Ak\(^{2}\)). Provided are structures (A) having formulas (Ia) to (Ib); (B) having formulas (Ic) and (Id); and (C) having formulas (Ie) to (If).

FIG. 3A-3B shows schematics of exemplary polymer structures having one or more functional groups including a cationic moiety (R\(^{2}\)) or functional groups including a halo group (R\(^{2}\)). Provided are structures (A) having formulas (Ig) to (Ih); and (B) having formulas (Ii) to (Ij).

FIG. 4A-4B shows schematics of exemplary polymer structures having R\(^{1\prime\prime}\) (i.e., a substituent that includes a cationic moiety or a halo group) and L\(^{-}\) (i.e., a linker, such as any herein). Provided are structures (A) having formulas (1-1) to (1-2); and (B) having formulas (1-3) to (1-4).

FIG. 5A-5B shows schematics of exemplary polymer structures having R\(^{4\prime}\) (i.e., a substituent that includes a cationic moiety) or R\(^{4\prime\prime}\) (i.e., a substituent that includes a
three R² substituents appended on three pendant aryl groups of the DAPP (e.g., in which R⁰ is —C(O)—Ar—R¹) and three R’ substituents appended on three other pendant aryl groups (e.g., in which R’ is —C(O)—Ar—R’). Additional reaction steps can be conducted to modify the linker. In one instance under reducing conditions, the carbonyl linker (—C(O)—) is reduced to a methylene linker (—CH₂—), thereby providing polymer (IV-4). This polymer is then reacted in the presence of a reagent (e.g., R⁴) to provide polymer (IV-5) including cationic moieties R⁴ that is —CH₂—Ar—R⁴, in which R⁴ is an anion) and halo groups (e.g., R⁵ that is —CH₂—Ar—R⁵, in which R⁵ is halo). Polymer (IV-4) can be cast as a film and then reacted with a reagent R⁴. Alternatively, polymer (IV-5) can be cast as a film.

Fig. 11 shows a schematic of an exemplary reaction scheme to provide polymer structure (IV-7). Provided is an exemplary reaction of a labeled Diels-Alder poly(phenylene) polymer (labeled “F-labeled DAPP”) in the presence of a reagent (e.g., R⁷—X such as CF₃—Ar—C(O)—Cl) to form a DAPP (IV-6) having two reactive handles R⁷ appended to two pendant aryl groups of the DAPP (e.g., in which R⁷ is —C(O)—Ar—CF₃); and then a further reaction of a R⁸-containing DAPP in the presence of a reagent (e.g., R⁸—X such as CICH₂—Ar—C(O)—Cl) to form a DAPP (IV-7) having a functional group R⁹ attached to other pendant aryl groups (e.g., in which the R⁹ is —C(O)—Ar—CH₂Cl).

Fig. 12 shows a schematic of an exemplary reaction scheme to provide polymer structure (IV-8). Provided is an exemplary reaction of a DAPP (IV-7, provided as a cast film) with a reagent (e.g., Na(CH₃)₂) to provide polymer (IV-8) including cationic moieties (e.g., R⁸ that is —C(O)—Ar—CH₂—N(CH₃)₃, in which Ar is phenyl) and halo groups (e.g., R⁹ that is —CH₂—Ar—CF₃, in which Ar is phenyl). Additional reaction steps can be conducted to modify the linker. In one instance under reducing conditions (e.g., with HSiEt₃), the carbonyl linker (—C(O)—) is reduced to a methylene linker (—CH₂—), thereby providing polymer (IV-9). This polymer is then reacted in the presence of a reagent (e.g., Na(CH₃)₂) to provide polymer (IV-10) including cationic moieties (e.g., R⁸ that is —CH₂—Ar—CH₂—N(CH₃)₃, in which Ar is phenyl) and halo groups (e.g., R⁹ that is —CH₂—Ar—CF₃, in which Ar is phenyl). Polymer (IV-10) can then be cast as a film.

Fig. 15 shows another exemplary polymer structure (IV-11) including cationic moieties (e.g., R⁸ that is —Ak—N(CH₃)₃, in which Ak is allylalkene) and halo groups (e.g., R⁹ that is —CH₂—Ar—CF₃, in which Ar is phenyl).
groups (R"'), thereby providing a further functionalized polymer structure having formula (IX). FIG. 23A-23C shows schematics of exemplary polymer structures having one or more reactive handles (R"'). Provided are (A) an exemplary schematic of various portions of the DAPP that can be appended with a reactive handle R" (e.g., on one or more pendant groups of DAPP) or with an acidic group (e.g., on the backbone and/or one or more pendant groups of DAPP). Also provided are exemplary polymer structures (B) having formulas (IIk) to (IIp) and (C) having formulas (IIq) and (Irr). Any of the reactive handle R" in this figure can be reacted with a reagent to provide a R"G group.

FIG. 24 shows schematics of exemplary polymer structures having formulas (II-7) to (II-12), which include one exemplary reactive handle R" on a pendant aryl group ArI. Any of the fluoro groups in this figure can be reacted with a reagent to provide a cationic moiety. Alternatively, the fluoro group can be maintained for use as a R" group. FIG. 25A-25C shows exemplary reaction schemes involving Diels-Alder polyphenylene polymers (DAPPs). Provided are (A) an exemplary reaction scheme for reacting DAPP to conduct a Friedel Crafts alkyl acylation reaction, thereby producing an alkyl acylated DAPP that can be further reacted to provide a cationic moiety as a R" group or maintained as a R" group; (B) exemplary reaction schemes for reacting DAPP to conduct a Friedel Crafts aryl acylation reaction; and (C) an exemplary reaction scheme showing the reaction between a silver triflate reagent (AgOTf) and a benzoyl chloride, a potential source for a reactive handle, and then further functionalization with a phenyl group of a polymer.

FIG. 26A-26C shows reaction of a labeled DAPP in the presence of a reagent to provide a reactive handle. Provided are (A) an exemplary reaction scheme for reacting a F-labeled DAPP in the presence of a reagent (e.g., R"F-X, such as F—Ar—C(O)—Cl) to form a DAPP (II-13) having two reactive handles R" appended to two pendant aryl groups of the DAPP (e.g., in which R" = F—Ar—C(O)—Cl; (B) an NMR spectrum of the F-labeled DAPP; and (C) an exemplary reaction scheme for reacting a R"-containing DAPP in the presence of a reagent (e.g., R"—X, such as CH_2O—Ar—O—H) to form a DAPP (II-14) having a functional group R" attached to each of the two reactive handles R" (e.g., in which the reacted R" is —Ar—C(O)—Cl, and in which R" = CH_2O—Ar—O—H). Any of R" and R" in this figure can be reacted with a reagent to provide a R" group, or the R" group can be maintained to provide a R" group.

FIG. 27 shows an exemplary reaction scheme for reacting a F-labeled DAPP in the presence of a reagent (e.g., R"F-X, such as F—Ar—SO_2—C) and a metal salt (e.g., M(OTf) to form a DAPP (II-15) having nine reactive handles R" appended to six pendant aryl groups and three backbone aryl groups of the DAPP (e.g., in which R" = F—Ar—SO_2—C). Any of the reactive handle in this figure can be reacted with a reagent to provide a R" group, or the fluoro-containing group can be maintained to provide a R" group.

FIG. 28 shows an exemplary reaction scheme for performing a Diels-Alder reaction to generate the Diels-Alder poly(phenylene) (DAPP, 3*) and for performing a Friedel Crafts aryl acylation reaction to generate the DAPP having two reactive handles. Any of the reactive handle in this figure can be reacted with a reagent to provide a R" group, or the fluoro-containing group can be maintained to provide a R" group.

FIG. 29 shows further exemplary compounds having reactive handles. Provided is compound (II-17) having reactive handles (e.g., an R"', such as an optionally substituted arylalkyl in combination with acidic moieties (e.g., an R" group, such as —SO_2H). Also provided is compound (II-18) having various types of reactive handles (e.g., an R"', such as an optionally substituted alkaryl group that is substituted with an aminoalkyl group and/or an optionally substituted alkaryl group that is substituted with a perfluoroalkyl group). For compound (II-18), each Ar is independently, an optionally substituted alkyl group (e.g., such as methylene, ethylene, etc.). In each of these compounds, in can be any useful number (e.g., any herein, such as of from about 40 to about 100). Any of the reactive handle in this figure can be reacted with a reagent to provide a R" group, or the fluoro-containing group can be maintained to provide a R" group.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to polymer structures having various functional groups including a cationic moiety or a halo group (e.g., a R" group). In particular embodiments, R" is a functional group including the cationic moiety, and R" is a functional group including the halo group. The R" groups can be provided on any useful site of the underlying polymer (e.g., pendant groups and/or backbone groups of the polymer). In some embodiments, the polymer includes both R" groups and R" groups (e.g., R" and R" on pendant groups and/or backbone groups of the polymer). Described herein are structures for such polymers having cationic moieties or halo groups, as well as methods for making and functionalizing such polymers.

Polymers

The present invention encompasses polymers, including copolymers. Exemplary polymer include any described herein, such as non-limiting generic structure provided in formulas (I), (In), (Ie), (Id), (Ic), (Ib), (Ia), (I), (II), (III), (IV), (V), (VI), (VII), (VIII), (IX), as well as particular structures provided as structures (I-1), (I-2), (I-3), (I-4), (I-5), (I-6), (I-7), (I-8), (I-9), (I-10), and (I-11) (see FIGS. 1, 2A-2C, 3A-3B, 4A-4B, 5A-5B, 6A-6B, 7A-7B, 8A-8B, 9A-9B, 10A-10B, 11A-11B, 12A-12B, 13A-13B, and 14A-14B), including salts thereof and forms thereof including a counter ion.

Of these, formulas (VI), (VII), (VIII), (IX), and (X) are considered to be reagents having one or more reactive end groups. Formula (VII) is considered to be a copolymer. In particular embodiments, the copolymer of the invention includes a first segment, a second segment, and at least one linking segment connecting at least one first segment with at least one second segment. The second segment can be a hydrophilic segment or a hydrophobic segment. The first segment can include at least one R" group.

In one embodiment, a polymer includes the structure of formula (I), including salts thereof and forms thereof including a counter ion. As can be seen in FIG. 1, formula (I) is a generic structure encompassing other structures (e.g., formula (In)). The polymer can include any useful number of R" on pendant aryl groups (e.g., aryl groups in formula (I) having an optional R" group) and/or backbone aryl groups (e.g., aryl groups in formula (I) having an optional R" group or R" group). The polymer can include any useful type of R" groups (e.g., R" including a cationic moiety or R" including a halo group), as well as any useful number of such groups (e.g., a groups, where a can in 0, 1, 2, 3, 4, or 5, and/or where at least one a is not 0).
The polymer can include any useful type of pendant substituents (e.g., substituents R\textit{1}, R\textit{2}, R\textit{3}, R\textit{4}, and/or R\textit{5}) on a pendant aryl group, such as those labeled with an R\textit{6} in formula (I) of FIG. 1 or with Ar1-Ar6 in formula (I-3) or (I-4) of FIG. 4B, as well as any useful number of such substituents on each aryl group (e.g., a substituents for R\textit{1}, R\textit{2}, R\textit{3}, R\textit{4}, and/or q substituents for R\textit{5}), where each of a and q is, independently, 0, 1, 2, 3, 4, or 5, and/or where at least one a is not 0. For any structure described herein, each R\textit{1} is, independently, a functional group R\textit{1} (e.g., R\textit{1} or R\textit{2}, R\textit{0}, or any described herein), an electron-withdrawing moiety (e.g., R\textit{2} or any described herein), or an inert substituent (e.g., H, halo, optionally substituted alkyl, optionally substituted alkoxy, etc.). In some embodiments, each and every R\textit{1} is, independently, R\textit{1} (e.g., R\textit{1} or R\textit{2}, R\textit{0}, or R\textit{2}), R\textit{0}, R\textit{0}, R\textit{0}, R\textit{0}, R\textit{0}, R\textit{0}, R\textit{0}, or R\textit{0}. In some embodiments, fully substituted pendant groups (e.g., R\textit{2} is not H) provide polymers with enhanced proton conductivity, enhanced anion exchange capability, and durability characteristics.

The polymer can also include any useful backbone structure. For instance, in formula (I), the backbone includes three groups, i.e., two R\textit{2}-substituted aryl groups and a bridging group Ar\textit{0} optionally including a functional group R\textit{3}. The polymer can include any useful type of backbone substituents (e.g., backbone substituents R\textit{1} or R\textit{2} disposed on a backbone aryl group), as well as any useful number of such substituents on each group (e.g., a substituents for R\textit{1}, R\textit{2}, and/or q substituents for R\textit{2}), where each of a and q is, independently, 0, 1, 2, 3, 4, or 5, and/or where at least one a is not 0. For any structure described herein, each R\textit{2} is, independently, a functional group (R\textit{4}, R\textit{4}, or R\textit{4}), an acidic moiety (e.g., R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, or R\textit{4}), an electron-withdrawing moiety (e.g., R\textit{5} or any described herein), or an inert substituent (e.g., H, halo, optionally substituted alkyl, optionally substituted alkoxy, etc.). In some embodiments, each and every R\textit{2} is, independently, R\textit{2} (e.g., R\textit{2} or R\textit{2}, R\textit{2}, R\textit{2}, R\textit{2}, R\textit{2}, or R\textit{2}). Each of bridging group Ar\textit{0} and connecting group Ar\textit{M} can be any useful bivalent linker. In particular embodiments, each of Ar\textit{0} and Ar\textit{M} is, independently, includes an optionally substituted arylene group. In some embodiments, each of Ar\textit{0} and Ar\textit{M} is, independently, an optionally substituted arylene group. In other embodiments, each of Ar\textit{0} and Ar\textit{M} is, independently, substituted with one, 2, 3, or 4 R\textit{3} substituents, R\textit{3} substituent(s), R\textit{3} substituent(s), R\textit{3} substituent(s), R\textit{3} substituent(s), or label(s). Exemplary labels include a detectable label, such as an NMR label (e.g., fluorine, such as 13C; nitrogen, e.g., 15N; or oxygen, e.g., 18O), a spin label, an isotopic label, a mass label, a fluorescent label, a dye, etc.

In yet other embodiments, each of Ar\textit{0} and Ar\textit{M} is, independently, configured to reduce meta linkages. Thus, in some instances, each of Ar\textit{0} and Ar\textit{M} is, independently, a bivalent linker formed by removing a hydrogen atom from opposite faces of an aryl group. Examples of such linkers include 1,4-benzenediyl (or 1,4-phenylene), 2,7-phenanthrylene (or 2,7-phenanthrenediyl), 1,5-naphthalene (or 1,5-naphthalenediyl), etc. For example, the polymer can include a structure of Formula (I) but having Ar\textit{0} as a R\textit{3}-substituted 1,4-phenylene and Ar\textit{M} as an R\textit{3}-substituted 1,4-phenylene, an R\textit{4}-substituted 1,4-phenylene, an R\textit{4}-substituted 1,4-phenylene, an R\textit{3}-substituted 1,4-phenylene, or an R\textit{3}-substituted 1,4-phenylene.

A polymer can include any useful number of structures of formula (I). In some embodiments, the polymer includes in structures, where n is an integer of from about 1 to 1000 (e.g., from about 1 to 500). Functional groups R\textit{4} can be present on the same polymer or on the same segment of the polymer with any other different type of substitutions, e.g., reactive handle substitutions (e.g., R\textit{4}), acidic substitutions (e.g., R\textit{4}, R\textit{4}, R\textit{4}, and/or R\textit{4}, as well as combinations thereof) and R\textit{4} substitutions. In particular embodiments, R\textit{4} groups can be employed to install functional groups to promote binding to an anion, and R\textit{4} groups can be employed to provide hydrophobic characteristics. In other embodiments, the use of acidic moieties and electron-withdrawing moieties could provide orthogonal chemistries to control and optimize performance (e.g., by employing acidic moieties to control ion conduction) and durability (e.g., by employing electron-withdrawing moieties to reduce oxidation). Further, the presence of a reactive handle R\textit{4} allows the polymer to be further functionalized (e.g., with one or more functional groups R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, R\textit{4}, and/or R\textit{4}, as well as any other groups described herein). In one instance, each pendant aryl group is substituted with an R\textit{4} (e.g., an R\textit{4} and/or an R\textit{4}), an R\textit{4}, an R\textit{4}, an R\textit{4}, an R\textit{4}, or an R\textit{4}. Optionally, one or more arylene groups can be further substituted with an R\textit{4} (e.g., an R\textit{4} and/or an R\textit{4}), an R\textit{4}, an R\textit{4}, an R\textit{4}, and/or an R\textit{4}.

As seen in FIG. 2A, formulas (Ia) and (Ib) provide polymers having different representations of the R\textit{4} functional group. As can be seen, formula (Ia) includes a R\textit{4} moiety in which each moiety includes a linker L\textit{4} and an optionally substituted aryl group Ar\textit{4} including a cationic moiety or a halo. As seen in formula (Ib), the R\textit{4} moiety includes a linker L\textit{4} and an optionally substituted alkyl group Ak\textit{4} including a cationic moiety or a halo. Linker L\textit{4} can include any useful linker moiety described herein, such as a covalent bond, carboxyl, oxy, thio, azo, phosphon, phosphonyl, sulfonyl, sulfonyl, sulfonamide, imino, imine, phosphine, nitrilo, optionally substituted C\textsubscript{1-12} alkylene, optionally substituted C\textsubscript{1-12} alkyleneoxy, optionally substituted C\textsubscript{1-15} heterocyclyl, optionally substituted C\textsubscript{1-15} heterocyclylxy, optionally substituted C\textsubscript{4-18} arylene, or optionally substituted C\textsubscript{4-18} aryleneoxy.

The aryl group Ar\textit{4} can be any useful aryl group (e.g., any herein, such as phenyl, benzyl, etc.) that is optionally substituted (e.g., any herein described for an aryl group) and that also includes either a cationic moiety (e.g., any herein, such as an ammonium cation, a sulfonyl cation, a phosphonium cation, an oxonium cation, a diazonium cation, or a halonium cation) and/or a halo (e.g., any herein, such as fluoro, chloro, bromo, or iodo). The alkyl group Ak\textit{4} can be any useful alkyl group (e.g., any herein, such as methyl, propyl, butyl, etc.) that is optionally substituted (e.g., any herein described for an alkyl group) and that also includes either a cationic moiety (e.g., any herein, such as an ammonium cation, a sulfonyl cation, a phosphonium cation, an oxonium cation, a diazonium cation, or a halonium cation) and/or a halo (e.g., any herein, such as fluoro, chloro, bromo, or iodo).

The R\textit{4} moiety can be present on any useful sites within a polymer. As seen in FIG. 2B, formulas (Ic) and (Id) provide polymers having R\textit{4} functional groups on pendant aryl groups (e.g., a number of \textit{L}-Ar\textit{4} groups on pendant aryl groups of formula (Ic) and a number of \textit{L}-Ak\textit{4} groups on pendant aryl groups of formula (Id)). As seen in FIG. 2C, different combinations of R\textit{4} moieties including aryl and alkyl groups are present on the same polymer. For
instance, formula (Ie) provides a polymer having both \(-L^2\)-Ar groups and \(-L^1\)-Ak groups on backbone and pendant aryl groups. In another instance, formula (II) provides a polymer having both \(-L^2\)-Ar groups and \(-L^1\)-Ak groups on pendant aryl groups.

An R² group can either be a functional group including a cationic moiety (e.g., R²) or a functional group including a halo (e.g., R²) and a polymer can have any useful combination of R² and R⁴ groups. As seen in FIG. 3A, formula (Ig) includes a cationic R² group on three pendant aryl groups, a halo-containing R² group on three other pendant aryl groups, and an R⁴ group on backbone aryl groups. Formula (Ih) includes a cationic R² group on three pendant aryl groups, as well as a halo-containing R² group on three other pendant aryl groups. As seen in FIG. 3B, formula (Ii) includes a cationic R² group on four pendant aryl groups, a halo-containing R² group on two pendant aryl groups, and an R⁴ group on backbone aryl groups. Formula (Ij) includes a cationic R² group on four pendant aryl groups, as well as a halo-containing R² group on two pendant aryl groups.

FIG. 29 provides an exemplary polymer of formula (II-18) having a functional group with a cationic moiety (R², e.g., \(-Ak-Ph-Ak-NMe₂\)) and a functional group including a halo (R², e.g., \(-Ak-Ph-CF₃\)).

Polymer Reagents
The present invention also includes reagents having any useful polymer segment described herein. For instance, the reagent can include a polymer segment disposed between two reactive end groups, where each end group can be the same or different. The polymer segment can be any described herein (e.g., a structure provided in formula (I), (Ia), (Ib), (Ic), (Id), (Ie), (If), (Ig), (Ii), (Ij), (I1), (Ii1), (Iib), (Iib), (Iid), (II), (III), (IV), (V), (VII), (VIII), (VII), (VIII), (IX), (XI), as well as specific structures provided as structures (I-1), (I-2), (I-3), (I-4), (I-5), (I-6), (I-7), (I-8), (IV-3), (IV-5), (IV-8), (IV-10), and (IV-11)). In addition, the polymer segment can include a second segment (e.g., Ar²), as any described herein.

Optionally, a sublink L can be present between the polymer segment and a reactive end group. The sublink L can be composed of any useful linkage, such as any described herein (e.g., those described for linking segment L).

The reactive end group can be any useful group configured to react with a second reactive end group. In this way, ordered copolymer block structures can be synthesized by selectively placing reactive end groups on the ends of blocks or segments to form polymer reagents, and then reacting that polymer reagent to place the segments in an end-to-end fashion in the copolymer. A skilled artisan would understand how to place reactive end groups in a polymer reagent in order to form a copolymer with the desired configuration or order.

The reactive end group is usually placed on the ends of a first polymer reagent, as well as on the ends of the second polymer reagent. Then, a first reactive end group on the first polymer reagent reacts with the second reactive end group on a second polymer reagent. The first and second reactive end groups can be chosen from a pair of co-reactive groups. For example, such pairs of co-reactive groups include (i) a nucleophile for use with (ii) an electrophile; (i) an optionally substituted aryl group (e.g., having a —C(O)R² group, where R² is an aryl group having one or more halo) for use with (ii) an optionally substituted aryl group (e.g., having a —OR² group, where R² is an aryl group having one or more halo) that can be deprotected prior to conducting a reaction; (ii) an optionally substituted aryl group (e.g., having a —C(O)R² group, where R² is an aryl group having one or more halo) for use with (ii) an optionally substituted alkyloxy group (e.g., such as —OR⁴, where R⁴ is H or an O-protecting group that can be deprotected prior to conducting a reaction); (i) an optionally substituted aryl group for use with (ii) an optionally substituted alkyloxy group (e.g., such as —OR⁴, where R⁴ is H or an O-protecting group that can be deprotected prior to conducting a reaction); (i) an optionally substituted alkynyl group for use with (ii) an optionally substituted azido group, which can participate in a Huisgen 1,3-dipolar cycloaddition reaction; as well as (i) an optionally substituted diene having a 4π electron system for use with (ii) an optionally substituted diene having an optioned sublink L', which can participate in a Diels-Alder reaction. For the co-reactive groups above, reagent (i) reacts with reagent (ii) in each pair. In one instance, the reactive group is R² (e.g., any described herein).

An exemplary polymer reagent is provided as structure (VI) in FIG. 18A. As can be seen, polymer reagent (VI) includes a two reactive end groups R² with a polymer segment (in brackets) placed between the reactive end groups. For this exemplary reagent, the optional sublink L' is located between the polymer segment and one of the reactive end groups. For reagent (VI), the polymer segment is that of formula (I), but any formula or structure herein can be employed for this polymer segment.

Further exemplary polymer reagents are provided as structure (VII) to (VId) in FIG. 18A-18C. Exemplary reagents include a polymer having structure (VIIa) to (VId), which includes a sublink having a structure similar to that of formula (I) but lacking aryl group Ar⁴.

Copolymers
The present invention also includes copolymers. In one embodiment, the copolymer includes the structure of formula (VII), including salts thereof. As can be seen in FIG. 21A, formula (VII) is a generic structure. Similar to formula (I) described above, the copolymer structure includes R⁴-substituted pendant and/or backbone aryl groups, R¹-substituted aryl groups, bridging group Ar², connecting group Ar³, pendant substituents R⁴, and m units. Thus, the description for these substituents provided for formula (I) applies equally to formula (VII). In some embodiments, each of Ar² and Ar³ is, independently, an optionally substituted phenylene. In other embodiments, each of Ar² and Ar³ is, independently, an optionally substituted 1,4-phenylene, e.g., Ar² as a 1,4-substituted 1,4-phenylene and/or Ar³ as a 1,4-substituted 1,4-phenylene.

FIG. 21B provides formula (VIII), which is another generic structure including a first segment, a linking segment, a second segment, and two reactive end groups R². The first segment can be any described herein (e.g., a structure having formula (I)). The reactive end group R² can be any described herein. As seen in FIG. 21C, the structure of formula (VIIia) includes a reactive end group R² that is an optionally substituted aryl group (e.g., an aryl group having a number of R⁴ groups).

Formulas (VII) and (VIII) also include additional groups, including a linking segment L and a second segment Ar⁴ of n units. The linking segment L can be any useful linkage (e.g., any herein), including those to form a covalent bond between the two segments. In some embodiments, the linking segment includes those composed of structures, or a portion of such structures, in the first segment and/or the second segment. Exemplary linking segments L include a covalent bond, an optionally substituted alkylene, an option-
ally substituted heteroalkylene, an optionally substituted alkyleneoxy, an optionally substituted heteroaryleneoxy, an optionally substituted arenylene, an optionally substituted aryleneox, an Ar unit, or a structure of formula (I).

The copolymer having formulas (VII) and (VIII) can have any useful second segment Ar". In some embodiments, Ar" includes a structure of formula (I) (e.g., where each R is H, optionally substituted alkyl, or R"; or where the number of R" substituents in Ar" is less than the number of R2 and/or R" substituents in the hydrophobic segment); a hydrophobic subunit; a sulfone subunit (e.g., a subunit including an --SO2-- group); an arylene sulfone subunit (e.g., --(Ar)2SO2--(Ar)3-- or --(Ar)2SO2--(Ar)4-- where Ar is an optionally substituted arylene group, as defined herein, and each a and b is an integer of about 0 to 10 and at least one of a or b is 1 or more); an ether sulfone subunit (e.g., --(X')3--SO2--(X')2--O-- or --X'--O--X'--SO2-- where each X' and X" is, independently, any useful group, such as optionally substituted arylene or optionally substituted alkylene, and each a and b is an integer of about 0 to 10 and at least one of a or b is 1 or more); an arylene ether sulfone subunit (e.g., --(Ar)2O--(Ar)3-- where Ar is an optionally substituted arylene group, as defined herein, and each a and b is an integer of about 0 to 10 and at least one of a or b is 1 or more); an arylene ketone subunit (e.g., --(Ar)C(O)--(Ar)2-- where Ar is an optionally substituted arylene group, as defined herein, and each a and b is an integer of about 0 to 10 and at least one of a or b is 1 or more); a perfluoroalkyl subunit (e.g., --(CF2)n--H, where n is an integer of 1 to about 16); or a perfluoroalkoxy subunit (e.g., --O(CF2)n--H, where n is an integer of 1 to about 18); or an arylene trifluoromethylenedioxy subunit (e.g., --O(CF2)n--O, where n is an integer of 1 to about 16), or an arylene trifluoromethylenedioxy subunit (e.g., --O(CF2)n--O(CF2)n--O, where n is an integer of 1 to about 16).

In some embodiments, formulas (VII) and (VIII) include a second segment Ar" that is a hydrophobic segment. In some embodiments, the second segment Ar" is a hydrophobic segment having one or more electron-withdrawing moieties (e.g., R") or one or more halo-containing functional groups (e.g., R") in particular embodiments, each pendant aryl group in the polymer or a segment thereof is substituted with an R2 substitution and/or an R2 substitution, where each substitution may be the same or different. In other embodiments, both pendant and backbone aryl groups are independently, substituted with an R2 substitution and/or an R2 substitution.

In other embodiments, formulas (VII) and (VIII) include a second segment Ar" that is a hydrophilic segment. In some embodiments, the second segment Ar" is a hydrophilic segment that includes the two R2-substituted aryl groups and a bridging group Ar'. Thus, in some embodiments, at least one substituent in this hydrophilic segment (e.g., substituents R1, R2, or R3) is a hydrophilic moiety (e.g., an acidic moiety, such as any R4, R5, R6, and/or R7 described herein or any moiety including a sulfonyle group or a phosphoryl group). In some embodiments, the hydrophilic segment includes one or more acidic moieties (e.g., R5, R6, and/or R7, as well as combinations thereof) on the pendant aryl groups. Exemplary hydrophilic segments include those having R4-substituted pendant aryl groups, R5-substituted pendant aryl groups, R6-substituted pendant aryl groups, and R7-substituted backbone aryl groups.

A copolymer can include any useful number or ratio of first and second segments (e.g., hydrophilic and hydrophobic segments). In some embodiments, formulas (VII) and (VIII) include m number of first segments (e.g., hydrophilic segments) and n number of second segments (e.g., hydrophobic segments), where each of m and n is, independently, an integer of from about 1 to 1000. In other embodiments, the m (the number of first segments) is minimized in order to minimize swelling of the copolymer. For example, in some instances, m≤n. In other instance, n is at least about 5 times greater than m (e.g., n is about 10 times greater than m, or n is about 20 times greater than m). In yet other instances, m is of from about 1 to 100, and n is of from about 5 to 500 (e.g., m is of from about 1 to 50, and n is of from about 5 to 500; m is of from about 1 to 50, and n is of from about 10 to 100; m is of from about 1 to 10, and n is of from about 5 to 500; m is of from about 1 to 20, and n is of from about 20 to 400; and m is of from about 1 to 10, and n is of from about 100 to 200). In some instances, m can be about 5.6 and n can be about 60.7 or 121.4. In other instances, m is of from about 1 to 20, and n is of from about 20 to 400.

For any polymer herein, including any copolymer herein, each and every R1 can be independently, R1", R2", R4", R5", R6", R7", R8", and/or R9". For instance, in some embodiments, each aryl group in the polymer or a segment thereof is substituted with an R2", an R4", an R5", an R6", an R7", R8", and/or an R9" substitution, where each substitution may be the same or different. Reactive handles R2" can be present on the same polymer or on the same segment of the polymer with any other different type of substitutions, e.g., acidic substitutions (e.g., R5", R6", and/or R7", as well as combinations thereof) and R8" substitutions. In particular, the use of acidic moieties and electron-withdrawing moieties could provide orthogonal chemistries to control and optimize performance (e.g., by employing acidic moieties to control ion conduction) and durability (e.g., by employing electron-withdrawing moieties to reduce oxidation). Further, the presence of a reactive handle R2" allows the polymer to be further functionalized (e.g., with one or more functional groups R2", R4", R5", R6", R7", R8", R9", and/or R10). In one instance, each pendant aryl group is substituted with an R2", an R4", an R5", an R6", an R7", an R8", and an R9", and/or an R10. Optionally, one or more backbone aryl groups can be further substituted with an R2", an R4", an R5", an R6", an R7", an R8", an R9", and an R10, and/or an R11.

Functional Groups and Moieties

The present invention includes the use of functional groups and moieties, such as functional groups (e.g., R4") including a cationic moiety (e.g., R4") or a halo (e.g., R4") reactive handles (e.g., R4"), acidic moieties (e.g., R5", R6", R7", and/or R8"), electron-withdrawing moieties (e.g., R9"), and other functional groups. Any number of these functional moieties can be present on the polymer (e.g., the polymer backbone aryl groups and/or pendant aryl groups).

Exemplary functional groups (e.g., R4") including any useful group including a cationic moiety (e.g., an anion, such as any described herein) or a halo (e.g., any described herein). In some embodiments, the functional group R4" includes --L4--Ar4" or --L4--Ak4", in which Ar4" is an optionally substituted aryl and in which Ak4" is an optionally substituted alkyl or optionally substituted heteroaryl. In particular embodiments, L4 is any useful covalent bond or any useful linker (e.g., any described herein). In some embodiments, Ar4" or Ak4" is substituted with one or more substituents selected from the group of halo, cyano, optionally substituted haloaryl, optionally substituted perfluoroalkyl, optionally substituted nitroaryl, and optionally substituted alkyl; and further includes a cationic moiety (e.g., an anion cation) or a halo (e.g., fluoro, or any described herein).

In some instances, the functional group R4" is a group including a linker R4 and a functional moiety R4" or R4" or R4". In particular embodiments, R4" is a cationic moiety or...
a halo. In some embodiments, R_4^1 is a cationic moiety or includes a cationic moiety (e.g., an ammonium cation, a sulfonium cation, a phosphonium cation, an oxonium cation, a diazonium cation, or a halonium cation). In other embodiments, R_5^1 is a halo or includes a halo.

In some embodiments, R_4^1 includes N^+. In other embodiments, R_4^1 is —N^+R_2^1R_2^2R_2^3, which includes —N^+R_2^1R_2^2R_2^3, where each of R_2^1, R_2^2, and R_2^3 is independently, H, optionally substituted alkyl, optionally substituted aryl, or optionally substituted alkenyl; or where R_2^1 and R_2^2, taken together with the nitrogen atom to which each is attached, form a heterocycle; or where R_2^1 and R_2^2, taken together, form an optionally substituted alkenyl or heteroaralkyl (e.g., as described herein). In some embodiments, each of R_2^1, R_2^2, and R_2^3 is independently, H or optionally substituted C_1-6 alkyl.

In some embodiments, R_4^1 includes S^-. In other embodiments, R_4^1 is —S^−R_2^1R_2^2R_2^3, which includes —S^−R_2^1R_2^2R_2^3, where each of R_2^1, R_2^2, and R_2^3 is independently, H, optionally substituted alkyl, optionally substituted aryl, or optionally substituted alkenyl; or where R_2^1 and R_2^2, taken together with the sulfonyl atom to which each is attached, form a heterocycle; or where R_2^1 and R_2^2, taken together, form an optionally substituted alkyl or heteroaralkyl (e.g., as described herein). In some embodiments, each of R_2^1 and R_2^2 is independently, H or optionally substituted C_1-6 alkyl.

In some embodiments, R_4^1 includes O^-. In other embodiments, R_4^1 is —O^−R_2^1R_2^2R_2^3, which includes —O^−R_2^1R_2^2R_2^3, where each of R_2^1, R_2^2, and R_2^3 is independently, H, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted aryl, or optionally substituted alkenyl; or where R_2^1 and R_2^2, taken together, form an optionally substituted alkyl or heteroaralkyl (e.g., as described herein). In some embodiments, each of R_2^1 and R_2^2 is independently, H or optionally substituted C_1-6 alkyl.

In some embodiments, R_4^1 is —N_2^+ or includes —N_2^+. In some embodiments, R_4^1 is —X^- or includes —X^-, where X is halo as defined herein. Exemplary halonium groups include an iodonium group (e.g., —I^-), a bromonium group (e.g., —Br^-), a chloronium group (e.g., —Cl^-), or a fluoronium group (e.g., —F^-).

In some embodiments, R_4^1 is halo or includes halo (e.g., F, Cl, Br, or I).

As seen in FIG. 4A, formulas (I-1) and (I-2) provide polymers having different representations of the R_4^1 functional moiety. As can be seen, formula (I-4) includes a R_4^1 moiety attached to the pendant aryl groups by way of an arylayl group (e.g., —C(O)—Ph). As can be also seen, formula (I-2) includes a R_4^1 moiety attached to the pendant aryl groups by way of a linker L_4 and a further aryl group (e.g., —L_4—Ph). The linker L_4 can be any useful bivalent linker. The R_4^1 moiety can be any useful functional group including a cationic moiety or halo (e.g., as described herein for R_4^1 or R_5^1).

A polymer can include any useful combination of R_4^1 groups, see, e.g., FIG. 4B. As can be seen, formula (I-3) includes a R_4^2 moiety attached to the pendant aryl groups by way of a linker L_4 alone or a linker with an aryl group, i.e., —L_4—Ph. R_4^2 groups can be provided any useful number of pendant aryl groups in any useful location. As can be also seen, formula (I-4) includes a R_4^3 moiety attached alternating pendant aryl groups by way of a linker L_4 or a further aryl group (e.g., —L_4—Ph). The linker L_4 can be any useful bivalent linker. The R_4^2 moiety can be any useful functional group including a cationic moiety or halo (e.g., as described herein for R_4^1 or R_5^1).

In any formula herein, the polymer includes a functional group in which the cationic moiety is distanced from the backbone. For instance, when R_4^2 is L_4—R_5^1, in which L_4 is a linker and R_5^1 is functional moiety including a cationic moiety, then L_4 is linker longer than three carbon atoms (e.g., an optionally substituted C_4-18 alkylene). Without wishing to be limited by mechanism, under high temperatures (e.g., greater than about 80°C), benzyl ammonium cations can degrade, and it has been postulated that the hydroxyl anions can nucleophilically attack the ammonium positive charge. Thus, a long alkyl tether can be employed to minimize such nucleophilic reactions, which may be explained by the increased steric bulk of the long alkyl chain that may wrap around the cation protecting it from nucleophilic attack.

Each R_5^1 functional moiety can be a functional moiety including a cationic moiety (R_4^1) or a functional moiety including a halo (R_5^1). Each of R_4^1 and R_5^1 can be located at any useful position of the pendant or backbone aryl groups, see, e.g., FIG. 5A. As can be seen, formula (I-5) includes four R_4^1 moieties attached to the pendant aryl groups by way of a linked aryl group (e.g., —L_4—Ph) and two R_5^1 moieties attached to the pendant aryl groups by way of another linked aryl group (e.g., —L_4—Ph). Formula (I-6) includes three R_4^1 moieties attached to the pendant aryl groups by way of a linked aryl group (e.g., —L_4—Ph) and three R_5^1 moieties attached to the pendant aryl groups by way of another linked aryl group (e.g., —L_4—Ph).

Functional moieties R_4^2 and R_5^1 can be attached to the polymer in any useful manner, see, e.g., FIG. 5B. As can be seen, formula (I-7) includes three R_4^2 moieties attached to the pendant aryl groups by way of a linker (e.g., —L_4) and three R_5^1 moieties attached to the pendant aryl groups by way of a linked aryl group (e.g., —L_4—Ph). Formula (I-8) includes three R_4^2 moieties and three R_5^1 moieties attached to alternating pendant aryl groups by way of a linker (e.g., —L_4) or a linked aryl group (e.g., —L_4—Ph).

Polymers having reactive handles R_4^2 can be further reacted to provide functional moieties R_4^2 on any useful polymer (e.g., a polymer having formula (I)). Exemplary reactive handles (e.g., R_4^2) include any useful group, such as H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted perfluoroalkyl, optionally substituted heteroalkyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted arylalkoxy, optionally substituted arylalkoxy, optionally substituted aryloxycarboxyl, optionally substituted aryloxycarboxyl, optionally substituted aryloxycarboxylalkyl, optionally substituted arylalkoxyalkyl, and optionally substituted arylalkoxyalkyl. In one instance, at least one R_4^2 includes an optionally substituted aryl group (e.g., an optionally substituted aryl group including a halo, a haloalkyl, a perfluoroalkyl, a hydroxyl, or an alkoxyl group).

In some embodiments, the reactive handle R_4^2 includes L_4—Ar or L_4—Ak with which Ar is an optionally substituted aryl and in which Ak is an optionally substituted alkyl or optionally substituted heteroalkyl. In particular embodi-
ments L" are any useful covalent bond or any useful linker (e.g., any described herein). In some embodiments, Ar" or Ak" is substituted with one or more substituents selected from the group of halo, cyano, optionally substituted haloalkyl, optionally substituted perfluoroalkyl, optionally substituted nitroalkyl, and optionally substituted alkyl.

FIG. 23B illustrates polymers having a structure that includes R" substituents selected from -L"-Ar" and -L"-Ak". As can be seen, the polymer can include one or more R" that is -L"-Ar". In some embodiments, the Ar" aryl-containing R" substituent is installed on each aryl group of the polymer (e.g., as in a structure having formula (Hk)). In other embodiments, the Ar" aryl-containing R" substituent is installed on each pendant aryl group of the polymer (e.g., as in a structure having formula (Hl)). In yet other embodiments, the Ar" aryl-containing R" substituent is installed on three pendant aryl groups of the polymer (e.g., as in a structure having formula (Hm)).

In some embodiments, the Ar" aryl-containing R" substituent is -L"-Ar", in which Ar" is an R"-substituted phenyl group. Furthermore, the number k of such R" substituents can be installed on each aryl group. R" can be any useful substituent, such as amino, azido, nitro, nitroso, halo, as well as any described for an aryl group (e.g., substituents (1)-(47) as defined herein for aryl). As seen in FIG. 23C, in other embodiments, the Ar" aryl-containing R" substituent is installed on three pendant aryl groups of the polymer (e.g., as in a structure having formula (Hj)).

In other embodiments, the Ar" aryl-containing R" substituent is -L"-Ar", in which L" is a sulfonil group and in which Ar" is a halo-substituted phenyl group (e.g., pentafluorophenyl, tetrafluorophenyl, trifluorophenyl, difluorophenyl, or monofluorophenyl). As seen in FIG. 23B, exemplary polymers include structures having formula (II-7) or structures having formula (II-8).

As can also be seen in FIG. 23B, the polymer can include one or more R" that is -L"-Ak". In some embodiments, the Ak" alkyl-containing R" substituent is installed on each aryl group of the polymer (e.g., as in a structure having formula (III)). In other embodiments, the Ak" alkyl-containing R" substituent is installed on each pendant aryl group of the polymer (e.g., as in a structure having formula (Hn)). In yet other embodiments, the Ak" alkyl-containing R" substituent is installed on three pendant aryl groups of the polymer (e.g., as in a structure having formula (Hp)).

In some embodiments, the Ak" alkyl-containing R" substituent is -L"-Ak", in which Ak" is an R"-substituted C1-alkyl group. Furthermore, any number h of such R" substituents can be installed on each aryl group, and any number h of -CR"R" substituent groups can be present within the R" substituent, in which each R" can be the same or different. R" can be any useful substituent, such as amino, amido, azido, nitro, nitroso, halo, as well as any described for an aryl group (e.g., substituents (1)-(27) as defined herein for aryl). As seen in FIG. 23C, in other embodiments, the Ak" alkyl-containing R" substituent is installed on three pendant aryl groups of the polymer (e.g., as in a structure having formula (Hr)).

In other embodiments, the Ak" alkyl-containing R" substituent is -L"-Ak", in which L" is a carbonyl group and in which Ak" is a halo-substituted alkyl group (e.g., perfluorophenyl, -(CF2)3CF, -(CH3)3CF, or -(CHF2)3CF, in which h is an integer of from about 1 to about 24). As seen in FIG. 24, exemplary polymers include structures having formula (II-11) or structures having formula (II-12).

Exemplary linkers (e.g., for L" or L") include a covalent bond, carbonyl (−C(O)−), oxo (−O−), phosphonoyl phosphonyl (−P(OH)−), phosphonyl (−P(O)<), sulfonyl (−SO2−), sulfoxyl (−SO−), sulfonamide (e.g., −SO−N−R−), −NR−SO2−, −SO2−NR−, or −NR−SO2−, where R is H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted alkoxy, optionally substituted aryl, or halo). In another instance, only the backbone aryl groups (i.e., aryl groups Ar7 to Ar9) are substituted (e.g., with one or more R", such as any herein). In yet another instance, the connecting group ArM labeled the ary group Ar10 is substituted (e.g., with one or more R", such as any herein). Optionally, the connecting group ArM can include a label (e.g., halo).

Any useful number of aryl groups in the polymer can include R". For instance, as seen in FIG. 19B, the polymer of structure (II-2) includes three pendant aryl groups, in which each of those pendant groups includes a R" substituent of −C(O)(p-R")-Ph. In some instances, each pendant aryl group is substituted. In other instances, only some of the pendant groups are substituted.

The polymer structure can include any useful combination of substituions, including one or more R" substituents in combination with one or more R" and/or R3 substituents. For
instance, as seen in FIG. 19C, the polymer of structure (II-4) includes four R^3 substituents (e.g., —C(O)—(p-R^4)—Ph located on pendant aryl groups), a R^1 substituent (e.g., —SO_2—H located on a backbone aryl group), and two R^2 substituents (e.g., —SO_3—H located on pendant aryl groups). Any useful number and type of R^4, R^5, and/or R^6 substituents can be present on a particular polymer structure. In another instance, the number q of R^3 substituent(s) is of from 0 to 5 for each aryl group (e.g., from 0 to 1, 1 to 5, 1 to 4, 1 to 3, 1 to 2, 2 to 5, 2 to 4, or 2 to 3). In one instance, the number h of R^4 substituent(s) is of from 0 to 5 for each aryl group (e.g., from 0 to 4, 0 to 3, 0 to 2, 0 to 1, 1 to 5, 1 to 4, 1 to 3, 1 to 2, 2 to 5, 2 to 4, or 2 to 3). In some embodiments, each aryl group includes one or more R^6. In other embodiments, one aryl group includes one or more R^4. In other embodiments, each pendant aryl group includes one or more R^5. In yet other embodiments, one to three pendant aryl groups includes one or more R^2. In other embodiments, each backbone aryl group or Ar^2 aryl group includes one or more R^5. In some embodiments, one backbone aryl group includes one or more R^4. In particular embodiments, each h for each aryl group is the same or different.

In another instance, each backbone aryl group or Ar^2 aryl group includes one or more R^5. In particular embodiments, each q for each aryl group is the same or different. In yet another instance, the number q of R^3 substituent(s) is of from 0 to 5 for each aryl group (e.g., from 0 to 1, 1 to 5, 1 to 4, 1 to 3, 1 to 2, 2 to 5, 2 to 4, or 2 to 3). In some embodiments, each pendant aryl group includes one or more R^5.

Any useful R^5 substituents can be present on any number of aryl groups (e.g., some of the pendant aryl groups, such as of from about 1 to about 3 pendant aryl groups). For instance, FIG. 20A provides another polymer of structure (II-5), which includes three pendant aryl groups (i.e., pendant aryl groups Ar1, Ar4, and Ar6) and in which each of these pendant groups includes a R^5 substituent of —C(O)—(R^6)—Ph. In another instance, FIG. 20B provides another polymer of structure (II-6), which includes three pendant aryl groups (i.e., pendant aryl groups Ar1, Ar4, and Ar6) and in which each of these pendant groups includes a R^5 substituent of —SO_2—(R^5)—Ph.

Other exemplary reactive handles R^3 include —SO_2—Ar^2, in which Ar^2 is an optionally substituted aryl (e.g., optionally substituted phenyl with one or more optional substituents selected from the group of halo, haloalkyl, nitro, nitroso, alkyl, etc.). In another instance, R^5 includes —SO_2—Ph, in which Ph is substituted with h1 number of R^1, where R^1 is selected from the group of halo, haloalkyl, nitro, nitroso, alkyl, etc., and where h1 is an integer of from 1 to 5.

Exemplary acyclic moieties (e.g., R^3) include any group having one or more sulfonyl groups, such as sulfo (e.g., —SO_2—OH), alkanolsulfonyl (e.g., —SO_2—R^3), where R^3 is optionally substituted C_1—C_12 alkyl), alkanolsulfonfylalkyl (e.g., —R^2—SO_2—R^3, where each of R^2 is optionally substituted C_1—C_12 alkene or optionally substituted heteroaralkyl and R^3 is optionally substituted C_1—C_12 alkyl), arylsulfonyl (e.g., —SO_2—R^3), where R^3 is optionally substituted C_1—C_12 aryl), arylsulfonfylalkyl (e.g., —R^3—SO_2—R^4—R^5—SO_2—R^6, where R^4 is independently, optionally substituted C_1—C_12 alkyl or alkene and R^5 is optionally substituted C_1—C_12 aryl), sulfonylalkyl (e.g., —SO_2—NR^3—R^4—R^5), sulfoamino (e.g., —N(R^4)—SO_2—R^3), aminosulfonyl (e.g., —SO_2—NR^3—R^4—R^5), or sulfonyl imide (e.g., —SO_2—NR^3—SO_2—R^3), where each of R^3 and R^5 is independently, optionally substituted C_1—C_12 alkyl (e.g., haloalkyl, such as perfluoroalkyl), optionally substituted C_4—C_18 aryl, or optionally substituted C_1—C_12 alkyl or optionally substituted C_1—C_12 alk—C_4—C_18 aryl; R^3 is H, optionally substituted C_1—C_12 alkyl (e.g., haloalkyl, such as perfluoroalkyl), hydroxy, optionally substituted C_1—C_12 alkylsulfonfyl, optionally substituted C_4—C_18 aryl, or optionally substituted C_1—C_12 alk—C_4—C_18 aryl; and R^5 is H, hydroxy, optionally substituted C_1—C_12 alkyl (e.g., haloalkyl, such as perfluoroalkyl), optionally substituted C_4—C_18 aryl, or optionally substituted C_1—C_12 alk—C_4—C_18 aryl.

In any of these moieties, each R^1 and R^3 is, independently, optionally substituted C_1—C_12 alkyl (e.g., haloalkyl, such as C_1—C_12 perfluoroalkyl), optionally substituted C_1—C_12 alkoxy, optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl; and R^5 is optionally substituted C_1—C_12 alk—C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl, optionally substituted C_1—C_12 alk—C_4—C_18 aryl optionally substituted C_4—C_18 aryl.
can be optionally substituted (e.g., with one or more substituents described for alkyl, as defined herein).

In any of these moieties, each of R'° and R'^° is, independently, optionally substituted C_{1-12} alkyl (e.g., haloalkyl, such as C_{1-2} perfluoroalkyl), optionally substituted C_{1-12} alkoxy, optionally substituted C_{1-18} aryl, optionally substituted C_{1-12} alkoxy, optionally substituted C_{4-18} aryl, optionally substituted C_{4-18} alkoxy, hydroxyl, or H; each of R''° is, independently, optionally substituted C_{1-12} alkyl, C_{1-18} aryl, or optionally substituted C_{4-18} aryl; and each R'''° is, independently, oxy, optionally substituted C_{1-12} alkylene, or optionally substituted heteroalkylene.

Yet other exemplary acidic moieties (e.g., R^°) include any group having a carboxyl group, such as carboxyl (e.g., —CO_{2}H), —C(O)—R', or —R'-C(O)—R' (e.g., where each R' is, independently, optionally substituted C_{1-12} alkyl (e.g., haloalkyl, such as C_{1-2} perfluoroalkyl), optionally substituted C_{1-12} alkoxy, optionally substituted C_{1-18} aryl, optionally substituted C_{1-12} alkoxy, optionally substituted C_{1-12} alkylene, or optionally substituted heteroalkylene).

Exemplary electron-withdrawing moieties (e.g., R^°) include optionally substituted C_{1-12} aryl, optionally substituted C_{6-18} aryl, carbonyl, optionally substituted C_{2-7} alkanoyl, optionally substituted C_{1-12} alkyl, optionally substituted C_{1-12} haloalkyl, optionally substituted C_{2-7} alkoxyalkyl, nitro, nitroso, cyano, sulfa carboxyl, and quaternary ammonium (e.g., —N'NR''N'R'''N'R''''), where each of R', R'', and R''' is, independently, optionally substituted alkyl, optionally substituted alkaryl, or optionally substituted aryl, or two of R', R'', and R''' taken together with the nitrogen atom to which each are attached, form a heterocyclic group, as defined herein). In another embodiment, R^° includes or is substituted by a C_{1-12} perfluoroalkyl group. In yet another embodiment, R^° is a C_{1-12} perfluoroalkyl group.

One or more functional groups can be appended to a reactive handle R'', Exemplary functional groups include any useful group, such as halo, nitro, nitroso, cyano, amino, amido, optionally substituted C_{1-12} alkyl, optionally substituted C_{1-12} haloalkyl, optionally substituted C_{1-12} perfluoroalkyl, optionally substituted C_{1-12} haloalkyl, optionally substituted C_{1-12} alkoxy, optionally substituted C_{1-12} alkoxyalkyl, optionally substituted aryloxy, optionally substituted aryloxycarbonyl, optionally substituted aryloxyl, optionally substituted aryloxysulfonylalkyl, and optionally substituted arylsulfonylalkyl, in addition to any that provides an R''^° (e.g., as defined herein). FIG. 22 provides a structure having the formula (IX) having h° number of R''^° substituents, in which R''^° includes a number a of reacted reactive handle R''^° (e.g., a reactive handle R''^°, such as any herein, lacking a leaving group (e.g., H, halo, etc.) that is covalently bonded to a functional group R''^° and includes a number h—a of non-reacted reactive handle R''^°, and in which a=a.

Any number of R^° substituents can include a functional group R^°. In one instance, every R^° is reacted with one or more R''^°, thereby providing a h° number of R''^° and in which h° is h). In another instance, some R^° is reacted with one or more R''^°, thereby providing a h° number of R''^° and in which h°=h.

The functional moieties including a cationic moiety, functional moieties including a halo, reactive handles, acidic moieties, electron-withdrawing moieties, and/or functional groups can be substituted or unsubstituted. For example, these groups can be substituted with one or more substitution groups, as described herein for alkyl and/or aryl.

Aryl Groups

The aryl groups herein can have any useful configuration, structure, and substitutions. Exemplary aryl groups (e.g., including arylenes, such as for Ar^{2}, Ar^{'2}, and Ar^{'a}) include the following groups, which may be optionally substituted:

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The diagram illustrates the various structures and groups mentioned in the text.
where each of \( Z, Z^1, Z^2 \), and \( Z^3 \) is, independently, \(-O-, \)

\(-S-\), \(-SO_2-\), optionally substituted alkylene, optionally substituted \( C_{1-12} \) alkoxylkene, optionally substituted \( C_{1-12} \) heteroalkylene,

\(-CF_2-\), \(-CH_2-OCF_2-\), \(-CF_2-\), perfluoralkylene,

\(-CF_2-\), \(-Si(R_1)(R_2)(R_3)-\), \(-R(O)(R')-\), \(-PR'-\), \(-C(O)-\), \(-C(CF_3)-\), \(-C(CH_3)-\), \(-CF_2-\), or \(-CCF_2Ph-\), and

where \( R' \) is \( H \), optionally substituted alkyl, or optionally substituted a methyl, ethyl, isopropyl, t-butyl, or phenyl.

**Polymer Salts and Forms Thereof Including a Counter Ion**

The present invention includes a salt or a form thereof including a counter ion of any polymer described herein, e.g., a salt or a form thereof including a counter ion of any one of formulas (I), (Ia), (Ib), (Ic), (Id), (Ie), (If), (Ig), (Ih), (Ii), (ii), (vi), (via), (vib), (vic), (vid), (vii), (viii), (villia), and (ix), as well as particular structures provided as structures (I-1), (I-2), (I-3), (I-4), (I-5), (I-6), (I-7), (I-8), (I-9), (I-10), and (I-11). In particular embodiments, the salt is a sodium salt. In other embodiments, the counter ion is an anion (e.g., a chloride anion or a hydroxide anion).

**Polymeric Starting Material**

Polymers having formula (II) can be employed as a starting material, in which reactive handles \( \text{R}^6 \) can be further reacted to provide functional moieties \( \text{R}^{6,4} \) on providing a polymer having formula (I). As can be seen in FIG. 16, formula (II) is a generic structure encompassing other structures (e.g., formula (Ia)), in which a polymer of formula (II) can be optionally synthesized from an initial polymer of formula (V). The polymer can include any useful number of reactive handles \( \text{R}^6 \) disposed on pendant aryl groups and/or backbone aryl groups. The polymer can include any useful type of pendant substrates (e.g., pendant substrates \( \text{R}^{6,4} \) and/or \( \text{R}^{6,5} \)), any useful number of such substrates on each aryl group (e.g., \( \text{h} \) substituents for \( \text{R}^{6,4} \) and/or \( \text{q} \) substituents for \( \text{R}^{6,5} \)), where each of \( h \) and \( q \) is, independently, 0, 1, 2, 3, 4, or 5, and/or where at least one \( h \) is not 0)

The polymer (e.g., of formula (II) or (V)) can include any useful type of pendant substrates (e.g., pendant substrates \( \text{R}^{6,4} \) and/or \( \text{R}^{6,5} \)), any useful number of such substrates on each aryl group (e.g., \( \text{h} \) substituents for \( \text{R}^{6,4} \) and/or \( \text{q} \) substituents for \( \text{R}^{6,5} \)), any useful number of such substrates on each group (e.g., \( \text{h} \) substituents for \( \text{R}^{6,4} \) and/or \( \text{q} \) substituents for \( \text{R}^{6,5} \)), where each of \( h \) and \( q \) is, independently, 0, 1, 2, 3, 4, or 5, and/or where at least one \( h \) is not 0).

Each of bridging group \( \text{Ar}^2 \) and connecting group \( \text{Ar}^{6,4} \) can be any useful bivalent linker (e.g., any described herein). In particular embodiments, each of \( \text{Ar}^2 \) and \( \text{Ar}^{6,4} \) is, independently, includes an optionally substituted aryl group. Furthermore, a polymer can include any useful number of structures of formula (I). In some embodiments, a polymer includes \( m \) structures, where \( m \) is an integer of from about 1 to 1000 (e.g., from about 1 to 500).

For any structure described herein, each \( \text{R}^3 \) or \( \text{R}^7 \) is, independently, a reactive handle \( \text{R}^{7,4} \), an acidic moiety (e.g., \( \text{R}^7 \), \( \text{R}^{7,5} \), or any described herein), an electron-withdrawing moiety (e.g., \( \text{R}^7 \) or any described herein), or an inert substituent (e.g., \( \text{H} \), optionally substituted alkyl, optionally substituted alkoxy, etc.). In some embodiments, each and every \( \text{R}^7 \) is, independently, \( \text{R}^{7,4} \), \( \text{R}^{7,5} \), \( \text{R}^7 \), \( \text{R}^{7,6} \), or \( \text{R}^7 \).

In other embodiments, each and every \( \text{R}^7 \) is, independently, \( \text{R}^{7,4} \), \( \text{R}^{7,5} \), \( \text{R}^7 \), \( \text{R}^{7,6} \), or \( \text{R}^7 \).

As seen in FIG. 17A, formulas (Ia) to (Ild) provide polymers having various combinations of structures for the bridging group \( \text{Ar}^2 \) and the connecting group \( \text{Ar}^{6,4} \). For example, formula (Ia) includes a connecting group \( \text{Ar}^{6,4} \); formula (Iib) includes a connecting group that is a \( \text{R}^7 \)-substituted 1,4-phenylene group; formula (Iic) includes a connecting group that is a \( \text{R}^7 \)-substituted 1,4-phenylene group; and formula (IIe) includes a bridging group that is a \( \text{R}^7 \)-substituted 1,4-phenylene group and a connecting group that is a \( \text{R}^7 \)-substituted 1,4-phenylene group. \( \text{R}^7 \) can be any substituent described herein. In some embodiments, each \( \text{R}^7 \) is, independently, \( \text{H} \), \( \text{halo} \), optionally substituted \( \text{C}_{1-12} \) alkyl, optionally substituted \( \text{C}_{1-12} \) haloalkyl, optionally substituted \( \text{C}_{1-12} \) perfluoralkyl, optionally substituted \( \text{C}_{1-12} \) heteroalkyl, \( \text{R}^7 \) (e.g., \( \text{R}^7 \) or \( \text{R}^{7,5} \)), \( \text{R}^7 \), \( \text{R}^7 \), or \( \text{R}^7 \).

As seen in FIG. 17B, formulas (Ile) to (Ili) provide polymers having various \( \text{R}^7 \) and \( \text{R}^{7,5} \) substituents on pendant aryl groups, as well as various \( \text{R}^7 \) and \( \text{R}^{7,5} \) substituents on backbone aryl groups. For instance, formula (Ile) provides a polymer having both \( \text{R}^7 \) and \( \text{R}^{7,5} \) substituents on some of the pendant aryl groups, whereas formula (Ilf) provides a polymer having either \( \text{R}^7 \) or \( \text{R}^{7,5} \) substituents on the pendant aryl groups. In other instances, formulas (Ilg) to (Ili) provide polymers having various levels of \( \text{R}^{7,5} \) substitution. As can be seen, formulas (Ilg) and (Ili) include \( \text{R}^{7,5} \) substituents on three of the pendant aryl groups. In another instance, formula (IIe) includes \( \text{R}^7 \) substituents on all pendant and backbone aryl groups, whereas formula (Ilf) includes \( \text{R}^{7,5} \) substituents on all pendant aryl groups.

Any polymer including an \( \text{R}^7 \) functional moiety can be employed as a starting material (e.g., any described herein, such as in FIGS. 16, 17A-17B, 19A-19C, 20A-20B, 22, 23A-23C, 24, 25A-25C, 26A-26C, 27, 28, and 29) to provide a polymer of formula (I). For instance, \( \text{R}^7 \) can be reacted with a functional agent to provide a functional moiety including a cationic moiety (e.g., an \( \text{R}^7 \) group). Alternatively, an \( \text{R}^7 \) group, if it includes a halo, can serve as a functional moiety including a halo (e.g., an \( \text{R}^7 \) group).

**Methods of Making Polymer Structures**

The polymers of the invention can be synthesized using any useful scheme. The following synthetic schemes are provided as non-limiting examples.

FIG. 8 shows an exemplary scheme in which a polymer including reactive handles \( \text{R}^{7,5} \) is further reacted to provide a polymer including functional moieties having cationic moieties \( \text{R}^7 \). As can be seen, an initial polymer (III) is reacted in the presence of a reagent (e.g., \( \text{R}^{7,5}X \)) to form a reactive polymer (IVa) having three reactive handles \( \text{R}^{7,6} \) appended to three pendant aryl groups. Then, reactive polymer (IVa) is treated with a further reagent (e.g., \( \text{R}^{7,5}X \)) to form a further reactive polymer (IVb) having three other reactive handles \( \text{R}^{7,6} \) appended to three other pendant aryl groups.
Finally, polymer (IVb) is treated with a reagent (e.g., R^6) to form a resultant polymer (II) having cationic moieties (R^4) and halo groups when R^5, when R^H is chosen to be a chemical moiety having a halo group). In this non-limiting manner, orthogonal chemistries can be installed on the same polymer structure.

In FIG. 8, the steps to install groups R^H and R^H can be combined into a single step or can be combined into a one-pot reaction in any useful order (e.g., in which reagent R^H — X is first introduced, and then reagent R^H — X is provided). Such groups can be selected to ensure that R^H displays increased reactivity to reagent R^4, as compared to R^H.

FIG. 9A-9C shows exemplary schemes for providing a functional moiety R^H on a poly(phenylene)-based polymer. FIG. 9A shows an exemplary reaction of a labeled Diels-Alder poly(phenylene) polymer in the presence of a reagent (e.g., R^4 — Ar — C — (O) — X) to form a DAPP (IV-1) having three R^H substituents appended on three pendant aryl groups of the DAPP (e.g., in which R^H is C(O) — Ar — R^H). Then, DAPP polymer (IV-1) is reacted with a second reagent (e.g., R^H — X), such as R^H — Ar — C — (O) — X to form a hydrophobic DAPP (IV-2) having three R^H substituents appended on three other pendant aryl groups of the DAPP (e.g., in which R^H is C(O) — Ar — R^H).

A functionalized polymer can be further reacted in any useful manner to provide a cationic, hydrophobic polymer (e.g., as a film). For instance, FIG. 9B shows hydrophobic polymer (IV-2), which was provided as a cast film and then reacted in the presence of a reagent (e.g., R^4) to provide polymer (IV-3) including cationic moieties (e.g., R^3 or R^3) and halo groups (e.g., R^5 or R^5). Alternatively, FIG. 9C shows a polymer in which a cationic moiety is formed and then the resultant polymer is then cast. As can be seen, polymer (IV-2) is reacted in the presence of a reagent (e.g., R^4) to provide polymer (IV-3) including cationic moieties (e.g., R^3 or R^3) and halo groups (e.g., R^5 or R^5). Then, polymer (IV-3) is cast as film. Furthermore, an anion exchange reaction can be conducted, thereby swapping R^H for any other useful anion (e.g., any described herein).

A functional group present on a polymer can be further reacted in any useful manner. In one instance, the linker includes an oxo group, which can be reduced with any useful reducing agent. As seen in FIG. 10, a polymer (IV-2) can include a carbonyl group, which can be reduced to a methylene group to provide polymer (IV-4). Furthermore, the polymer can be provided as a cast film and then reacted with an amine (reagent R^4) to provide a polymer (IV-5) including a plurality of cationic moieties.

As shown in Scheme I, the polymer of formula (IXa) can be formed by reacting a polymer of formula (I) having reactive handles, in which polymer (III) in turn can be formed by performing a Diels-Alder reaction to form the pendant and backbone aryl groups, and then performing a first substitution reaction to introduce R^H to the parent structure. These steps are described in more detail below.

First, a Diels-Alder reaction can be performed with an optionally substituted diene, such as a 1,4-bis-(2,4,5-triarylcyloalkylenediene)arylene reagent (1), with an optionally substituted dienophile, such as a diethylnylalkylene reagent (2). This reaction provides a Diels-Alder poly(phenylene) polymer (DAPP) (3). As can be seen, in this step, the number of subunits m is controlled by the stoichiometry of reagents (1) and (2).

Second, a substitution reaction is performed with reagent R^H — X with the DAPP product (3) to provide a substituted polymer (IIi), where X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate) and R^H is any described herein (e.g., R^H can be L-H-Ar^H or L-H-Ak^H).

Scheme I
The concentration of $R^{II}-X$ can be controlled to provide the desired extent of substitution on the DAPP pendant and/or backbone aryl groups. As can be seen, the number of $R^{II}$ substituents on each aryl group can be controlled by the stoichiometry of reagent $R^{II}-X$ and (DAPP) (3). In one instance, concentration can be controlled in order to install $R^{II}$ substituents on readily accessible pendant aryl groups. The reaction can be conducted until completion in order to access the backbone aryl groups, which are sterically more difficult to functionalize.

Optionally, the substitution reaction with reagent $R^{II}-X$ is performed in the presence of a metal salt and/or in the presence of an acid. Exemplary metal salts include M[O$_2$(SO$_2$-$R^{MF}$)], M[N(SO$_2$-$R^{MF}$)$_2$], or M[C(SO$_2$-$R^{MF}$)$_3$], where $R^{MF}$ is optionally substituted alkyl, optionally substituted aryl, optionally substituted alkaryl, optionally substituted haloalkyl, or perfluoroalkyl, and where M is Ag, Al, Ba, Bi, Ca, Cu, In, Re, Sc, Sn, Ti, Y, Yb, or Zn. Particular embodiments of metal salts include M[OTf]$_{m}$, where $m$ is an integer from 1 to 3 and where M is Ag, Al, Ba, Bi, Ca, Cu, In, Sc, Y, or Yb, as well as M[N(Tf)$_2$]$_{m}$, where $m$ is an integer from 1 to 3 and where M is Ag, Al, Sn, Ti, Yb, or Zn.

Exemplary acids include a Lewis acid or a Bronsted acid that acts as a catalyst, such as, e.g., HO(SO$_2$-$R^{IV}$), HO(SO$_2$-$R^{IV}$), HO(SO$_2$-$R^{IV}$), HO(SO$_2$-$R^{IV}$), and HO(CO(O)---R)$^{IV}$, where $R'$ is optionally substituted alkyl, optionally substituted aryl, optionally substituted alkaryl, optionally substituted haloalkyl, or perfluoroalkyl, and where $R''$ is optionally substituted aryl or optionally substituted alkaryl. Particular embodiments of acids include HO(SO$_2$CF$_3$), HO(SO$_2$F), H$_2$SO$_4$, HO(SO$_2$-(p-CH$_3$)Ph), or HO(COCl)$_2$.

Third, a substitution reaction is performed to react a reactive handle $R^{IV}$ in the presence of a functional agent $R^{IV*}$—X, thereby providing a functional group $R^{IV*}$. As seen in formula (IXa), $R^{IV*}$ is formed by a reacted $R^{IV}$ group (indicated by $R^{IV}'$) that is appended by a reacted functional moiety $R^{IV*'}$. In one non-limiting example, the reactive group $R^{IV}$ can be a -Ph-CH$_2$-Cl group that is reacted with an amine NR$_{N_1}$-R$^{N_2}$-R$^{N_3}$ (e.g., where each of $R^{N_1}$ and $R^{N_2}$ and $R^{N_3}$ is, independently, H or optionally substituted alkyl, or $R^{N_1}$ and $R^{N_2}$, taken together with the nitrogen atom to which each is attached, form a heterocyclic group, as defined herein), thereby providing an $R^{IV*}$ moiety of -Ph-CH$_2$-NR$_{N_1}$-R$^{N_2}$-R$^{N_3}$, in which reacted $R^{IV*}$ is -Ph-CH$_2$- and reacted $R^{IV*}$ is -NR$_{N_1}$-R$^{N_2}$-R$^{N_3}$.
As shown in Scheme II, the polymer of formula (II) can be formed by performing a Diels-Alder reaction to form the pendant and backbone aryl groups, performing a first substitution reaction to introduce R^3 to the parent structure, performing a second substitution reaction to introduce R^1, and performing a final substitution reaction to introduce R'^H. Polymer (II), in turn, can be reacted (e.g., by way of a substitution or replacement reaction) with a functional agent to provide a polymer of formula (I). The four steps to provide formula (II) are described in more detail below.

Similar to Scheme I, the first step in Scheme II includes a Diels-Alder reaction that is performed with an optionally substituted diene, such as a 1,4-bis(2,4,5-triphenyl cyclopentadienone)arylene reagent (1), in the presence of an optionally substituted dienophile, such as a diethynylarylene reagent (2). This reaction provides a Diels-Alder poly(phenylene) polymer (DAPP) (3).

The second step includes an initial substitution reaction, which is performed with reagent R^3—X in the presence of the DAPP product (3), thereby providing a substituted polymer (4). For reagent R^3—X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate) and R^3 is any described herein.

The third step includes a second substitution reaction, which is performed with reagent R^1—X in the presence of the substituted polymer (4) to provide the desired polymer of formula (I). For reagent R^1—X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate), and R^1 is any described herein.

Finally, the fourth step includes a third substitution reaction, which is performed with reagent R'^H—X in the presence of the DAPP product (3) to provide a substituted polymer (II). For reagent R'^H—X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate), and R'^H is any described herein (e.g., R'^H can be -L^1-Ar'^H or -L^2-Ak'^H).

The three substitution steps (i.e., the second, third, and fourth steps) can be performed in any order to obtain the
desired substitution pattern. Of course, if R^5 and R^1 are the same substituents, then only one of the substitution reaction steps can be conducted. Alternatively, one or more steps may be required to install R^1 or R^5 on the parent molecule. For instance, when R^1 or R^5 is --SO_2--NR^V Li--R^{S2}, multiple steps may be required to first install the --SO_2-- functional group on the parent molecule. Then, this functional group may be activated (e.g., by forming a sulfonyl halide, such as sulfonyl chloride) and reacted with an amine (e.g., NH--R^V Li--R^{S2}).

In another instance, an additional step may be required to install the functional group. For example, when R^1 or R^5 includes two sulfonyl groups, such as in --SO_2--NR--SO_2--R^{S2}, then sulfonyl groups can be attached sequentially. In one example, the method includes installing the first --SO_2-- functional group on the parent molecule and then reacted with a primary amine, such as NH_2R--SO_2, thereby providing a parent molecule having a --SO_2--NR^{V Li} sulfonyamide group. This sulfonyamide can then be reacted with an activated sulfonyl agent, e.g., a Cl--SO_2--R^{S2} agent, where R^{S2} is an optionally substituted C_1--C_12 alkyl, thereby providing an R^S moiety of --SO_2--NR^{V Li}--SO_2--R^{S2} on the polymer.

In yet another instance, when R^1 or R^5 is --R^{P Li}--P(O)<(R^{P Li}--R^{P Li}), multiple steps may be required to first install the R^{P Li} alkyne or heteroalkylene on the parent molecule, and then to later install the --P(O)<R^{S2}--R^{S2} group on the alkyne or heteroalkylene molecule. Furthermore, if R^{P Li} or R^{P Li} is an alkoxy or aryloxy group, then additional step may be required to modify a hydroxyl group attached to the phosphorous atom with an alkoxy or aryloxy group. A skilled artisan would understand that additional modifications or step can be employed to arrive at the desired structure.

Exemplary R^1--X and R^5--X reagents include HSO_2Cl, H_2SO_4, POCl_3, POCl_3, H_3PO_4, SO_3, fuming sulfuric acid, thionyl chloride, trimethylsilyl chlorosulfonate, dialky phosphites (e.g., diethyl phosphate with an optional catalyst, such as a Pd(0) catalyst), phosphines (e.g., tertiary phosphines), phosphoric acids (e.g., hypophosphorous acids, phosphonic acids, phosphinic acids, etc.), aryl halide (e.g., RX, where R is an optionally substituted aryl group, as defined herein, and X is halo), aryl halide (e.g., RX, where R is an optionally substituted aryl group, as defined herein, and X is halo, such as trifluorobenzoyl chloride), protein kinase (e.g., to install a phosphoryl group), phosphonyphenols, as well as mixtures thereof.

Scheme III

--- A^M === (2)
(-2 CO)
As discussed herein, the substitution steps can be performed in any useful order. In one non-limiting instance, the reaction scheme includes introducing one or more reactive handles R'''', and then introducing other substitution groups (e.g., R' and/or R''). As shown in Scheme III, the polymer of formula (II) can be formed by performing a Diels-Alder reaction to form the pendant and backbone aryl groups, performing a first substitution reaction to introduce R'''', performing a second substitution reaction to introduce R''', and performing a final substitution reaction to introduce R'. In one instance, the substitution steps including R''' and R'' can be conducted in the opposite order. These four steps are described in more detail below.

Similar to Schemes I and II, the first step in Scheme III includes a Diels-Alder reaction that is performed with an optionally substituted diene, such as a 1,4-bis-(2,4,5-triphenylcyclopentadienone)arylene reagent (1), in the presence of an optionally substituted dienophile, such as a diethylarylarylene reagent (2). This reaction provides a Diels-Alder poly(phenylene) polymer (DAAP) (3).

The second step includes a first substitution reaction, which is performed with reagent R''''-X in the presence of the DAAP product (3) to provide a R''''-substituted polymer (5). For reagent R''''-X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate), and R'''' is any described herein (e.g., R'''' can be L''''-Ar'''' or L''''-Ak'''').

The third step includes a second substitution reaction, which is performed with reagent R'''-X in the presence of the R''''-substituted polymer (5), thereby providing a R''''-,
R²-substituted polymer (6). For reagent R²—X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate) and R² is any described herein.

Finally, the fourth step includes a third substitution reaction, which is performed with reagent R¹—X in the presence of the R²—, R³-substituted polymer (6) to provide the desired polymer of formula (II). For reagent R¹—X, X is any useful leaving group (e.g., halo, hydroxyl, or sulfonate, such as mesylate, tosylate, or triflate), and R¹ is any described herein.
As shown in Scheme IV, the polymer reagent of formula (12) can be formed by performing a Diels-Alder reaction to form the pendent and backbone aryl groups and to install reactive end groups R₇. Then, substitution reactions can be performed in order to introduce R₁, R₃, and/or R₉. These three steps are described in more detail below.

Similar to that of Scheme I, the first segment is formed by performing a Diels-Alder reaction with a 1,4-bis-(2,4,5-triphenylcyclopentadienone)arylene reagent (1) and a diethynylarylene reagent (2).

To further install reactive end groups, the Diels-Alder reaction is also performed in the presence of a monoethynylarylene reagent (7). As can be seen, because reagent (2) includes two dienophile groups (i.e., two ethynyl groups), this reagent can react with two diene molecules (1), where the product of this reaction can further propagate the polymerization reaction. In contrast, reagent (7) includes only one dienophile group, and therefore terminates the polymerization reaction and provides a polymer reagent (8) having a terminal reactive end group R₇. Additional methods for installing reactive end groups are described in U.S. Pat. No. 8,110,636, which is incorporated herein by reference in its entirety.

Then, substitution reaction(s) can be performed. In Scheme IV, the substitution reactions are provided as three steps performed first with reagent R₇—X (e.g., as described herein) in the presence of an unsubstituted polymer (8) to form a further polymer (9), then with reagent R₃—X (e.g., as described herein) to form a further polymer (10), and finally with reagent R₉—X (e.g., as described herein) to form polymer reagent (12). If R₇ and R₃ are the same substituents, then a single substitution reaction step can be conducted. If R₇ and R₃ are different, then these substituents can be added in any desired order. A skilled artisan would understand that other modifications could be made to form the desired polymer reagent (12). In exemplary Scheme IV, Arₓ in formula (12) is Arₓ—(R₃)ₘ, which is a non-limiting embodiment.

Methods of making the polymer also include preparing an initial polymer having one or more R₇ and/or R₉ substituents, and then installing one or more R₉ on one or more pendent and/or backbone aryl groups. As seen in FIG. 23A, in one instance, the initial polymer is a sulfonated DAPP polymer (SDAPP) having one or more sulfo groups (e.g., on one or more pendant aryl groups), which can then be reacted with reagent R₉—X to install one or more R₉ substituents on that SDAPP polymer. As also seen in FIG. 23A, in another instance, the initial polymer is a fully sulfonated DAPP polymer (FS-DAPP) having one or more sulfo groups (e.g., on one or more pendant aryl groups and on one or more backbone aryl groups), which can then be reacted with reagent R₉—X to install one or more R₉ substituents on that FS-DAPP polymer.

In another instance, a precursor of the polymer herein (e.g., a polymer having a structure of formula (I)) is prepared as a membrane, and further functionalization is conducted to include one or more R₇, R₃, and/or R₉ substituents by reacting the membrane with one or more reagents to install such substituents.

Any reactions herein can be conducted with any useful reagent, solvent, or conditions. An example of reagent (1) includes 1,4-bis-(2,4,5-triphenylcyclopentadienone)benzene, and an example of reagent (2) includes diethynylbenzene reagent. Exemplary solvents useful for Diels-Alder and substitution reactions include an ether (e.g., diphenyl ether), methylene chloride, dichloroethane, etc. Salts of any poly-
mers can be obtained by reacting any product with a suitable acid or base to obtain the desired acid or base addition salt. Furthermore, additional reaction steps can be conducted to further purify, test, or use any polymer herein.


Uses

The polymers of the invention can be used in a variety of electrochemical applications. For instance, any polymer herein can be prepared as a membrane (e.g., by casting), and the membrane (e.g., a proton exchange membrane) can be incorporated into any device. In another instance, a precur-
sor of the polymer herein (e.g., a polymer having a structure of formula (1)) is prepared as a membrane (e.g., an ion exchange membrane), and further functionalization is conducted to include one or more R1 (e.g., R4 and/or R5), R2, R3, and/or R4 substituents by reacting the membrane with one or more reagents to install such substituents.

Exemplary devices include fuel cells (e.g., automotive fuel cells, hydrogen fuel cells, or direct methanol fuel cells), flow batteries (e.g., redox flow batteries, such as vanadium redox flow batteries), electrolyzers, electrochemical hydrogen production devices, etc. The membranes can be used for any use, such as a proton exchange membrane, an ion exchange membrane, a polymer separator, etc. In addition, the membranes can be in any useful form, such as a hydrogel. Membranes formed from the polymers herein can, in some instances, display enhanced properties, such as enhanced ion exchange capac-

EXAMPLES

Example 1: Fluorine-Containing Anion Exchange Membranes

Anion exchange membranes generally employ materials having a cationic charge in order to bind to anions. However, one recent hurdle in use of such anion exchange membranes in fuel cells has been the high water affinity of these materials due to the cationic charge. High water affinity results in poor fuel cell performance at high current density since the water created in the fuel cell is not rejected, and then blocks incoming hydrogen and air from reaching the catalytic sites. This results in flooding. We proposed using halo groups (e.g., fluoro) within the anion exchange polymer structure, which should improve the hydrophobic properties and resist flooding problems. One synthesis issue is that fluorine incorporation is typically difficult and require multi-step reactions.

Provided herein are compositions and methods including such halo-containing polymers that also include a cationic moiety, thereby enabling its use as an anion exchange membrane. We discuss methods to attach both fluorine and benzyl halide groups onto the Diels-Alder backbone. In FIG. 11, the first step is to attach the trifluorobenzoyl groups onto the poly(phenylene) backbone (e.g., catalyzed by triflic acid). The resultant polymer (IV-6) can be isolated and dried before the next step, but these reactions can be combined to a one pot (one step) process in which both acid chlorides are added at the same time. The synthesized polymer (IV-7) can include both the fluoro-containing functional groups and the chloro-containing functional groups. In FIG. 11, the fluorine in the poly(phenylene) backbone is not required but used herein as a reference for NMR characterization.

As seen in FIG. 12, the resultant polymer (IV-7) can be cast as a film and then soaked in aqueous trimethyl amine to provide a cationic polymer (IV-8). Alternatively, as seen in FIG. 13, the polymer (IV-7) can be dissolved in a solvent (e.g., tetrahydrofuran, THF), reacted with a trimethyl amine to provide the cationic polymer (IV-8), and then cast generate the trimethyl benzyl ammonium group.

Furthermore, any other useful synthetic steps can be employed to modify any portion of the polymer. In one
non-limiting instance, a ketone functional group can be sensitive to attack by a nucleophile (e.g., a hydroxide anion), and such a ketone group can be removed from the linker in any useful manner. In one instance, the ketone functional group is reduced prior to attaching the ammonium cation (Fig. 14), thereby providing intern polymer (IV-9) including chloro- and fluoro-groups that can be further reacted to provide a cationic polymer (IV-10). Any useful reagents can be employed. For example, for the reduction of ketone groups, refluxing in 1,2 dichloroethane (DCE) with triethyl silane and trifluoroacetic acid is sufficiently gentle to enable to minimize side reactions with the benzyl chloride groups. After reduction of the ketone, the resultant polymer can either be cast as a film or dissolved in a solvent (e.g., THF) to react with an amine (e.g., a trialkyl amine, such as NMe3) to form the ammonium cation.

A lengthy linker between the parent aryl group and the cationic moiety can also be incorporated by first attaching an alkyl chloride group in the optional presence of a Lewis acid (e.g., a 6-bromohexanoyl chloride in the presence of aluminum trichloride), then attachment of a halogen-containing aryl group in the presence of an acid catalyst (e.g., a trifluorobenzyl chloride with triflic acid), followed by ketone reduction, and then reaction with an amine to provide a cationic moiety (e.g., reaction with a trialkyl amine, such as NMe3). An exemplary polymer (IV-11) provided by such a synthetic scheme is provided in Fig. 15.

Example 2: Testing of Anion Exchange Membranes

Anion exchange membranes have been developed using poly(vinylidene) polymers formed by a Diels-Alder reaction (Diels-Alder polyvinylidene polymers, DAPPs). In particular, such a synthesis allows for use of poly(vinylidene) polymers as the backbone scaffold. FIG. 6A shows an exemplary poly(vinylidene)-based polymer, which displays high backbone stability under alkaline conditions (FIG. 7A). Without wishing to be limited by mechanism, the presence of aryl-aryl bonds provides a structure as these bonds are less likely to be cleaved, as compared to bonds within heterocum-compo-containing polymers, such as poly(aryl pseudophosphate) ethyl ethers (FIG. 6B). As can be seen, stress strain curves are provided for a DAPP (FIG. 7A) and a poly(aryl ether) (FIG. 7B) under varying alkaline conditions. The DAPP-based anion exchange polymer displayed enhanced mechanical stability under tested conditions, as compared to the poly(aryl ether) polymer. Accordingly, DAPP-based polymers display particular mechanical characteristics imparted by the backbone. It is believed that a DAPP-based polymer can be further modified to provide other chemical characteristics, such as by installing a cationic moiety to impart binding to anions or by installing a hydrophobic moiety (e.g., a halo) to provide a membrane with lower water affinity. Such polymer can, for instance, have a structure of formula (I).

Example 3: Functionalization of Diels-Alder Polyphenylene Polymers

Friedel-Crafts acylation reactions can be employed to functionalize Diels-Alder polyphenylene polymers (see, e.g., U.S. Pat. No. 8,809,483). Such functionalized polymers can be further reacted to provide any useful polymer (e.g., a polymer having formula (I)). As seen in FIG. 25A, a Diels-Alder polyphenylene polymer (DAPP) is functionalized by way of a Friedel-Crafts acylation reaction with an alkyl acyl chloride (e.g., 6-bromohexanoyl chloride) in the presence of aluminum trichloride as a catalyst, thereby providing an alkyl acylated DAPP.

When this Friedel-Crafts acylation approach was used to attach aryl acyl chlorides (e.g., benzoyl chloride), an insoluble product was obtained, which could not be processed further (FIG. 25B, top reaction pathway). Without wishing to be limited by mechanism, Lewis acids, such as FeCl3 and AlCl3, are known to catalyze oxidative carbon-carbon (C—C) coupling, including intramolecular and intermolecular C—C coupling, as well as aryl-aryl coupling, such as in a Scholl reaction. Such coupling reactions are not desired and may lead to insoluble polymeric products. Due to the insolubility of the product, provide by the reaction in FIG. 25B (top reaction pathway), we believe that only a trace amount of intramolecular or intermolecular C—C coupling of pendant aryl groups in DAPP would result in insoluble cross linking. Common trace impurities in AlCl3, such as FeCl3 and acidic protons, are potential catalysts for this process.

There are numerous differences between an alkyl acylation reaction (e.g., as in FIG. 25A) and an aryl acylation reaction (e.g., as in FIG. 25B). Without wishing to be limited by mechanism, the reaction pathway difference between alkyl and aryl acyl chlorides can be explained in terms of the stability of the acylammonium intermediates. An aryl acylammonium ion is stabilized by resonance delocalization, which is not available in alkyl acylammonium. Thus, the alkyl acylammonium ion is readily nucleophilically attacked by the pendant aryl groups of DAPP, while the aryl acylammonium ion reacts slower with the aryl groups so that it competes with aryl-aryl coupling (see, e.g., Corrò R et al., “Mécanisme de la C acylation: étude cinétique du mécanisme de l’acylamine des composés aromatiques catalysée par AlCl3,” Tetrahedron 1971; 27:5819-31; and Corrò R et al., “Mécanisme de la C acylation: étude cinétique du mécanisme de la benzoylation des composés aromatiques catalysée par AlCl3,” Tetrahedron 1971; 27:5601-18). Due to these differences in stability between the alkyl-based versus aryl-based ions, different reaction pathways and different end-products can be observed.

New strategies were required to effectively attach aryl-based functional groups on DAPP backbone and/or pendant groups. In particular, these developments included use of a metal salt to promote aryl acylation. Effnerberger published work discussing non-metal catalyst, Friedel Crafts acylation employing silver triflate (see Effnerberger F et al., “Trifluoromethanesulfonic-carboxylic anhydrides, highly active acylation agents,” Angew. Chem. Int’l Ed. 1972; 11(4):299-300). Without wishing to be limited by mechanism, a reaction between silver triflate and benzoyl chloride generally generates a trifluoromethanesulfonic-carboxylic anhydride and silver chloride (FIG. 25C). The anhydride can then further react with aromatic such as benzene or a phenylo group to form benzophenone at high yields (e.g., a yield of about 90% or greater). One disadvantage of utilizing silver triflate in this manner is that for every aryl acyl chloride, at least one equivalent of silver triflate is required. An alternative to silver triflate, is employing triflic acid; only a catalytic amount (e.g., 1%) can be used for the Friedel Crafts acylation of aryl acyl chlorides (see, e.g., Effnerberger F et al., “Catalytic Friedel-Crafts acylation of aromatic compounds,” Angew. Chem. Int’l Ed. 1972; 11(4):300-1).

We have applied this chemistry onto a Diels-Alder polyphenylene (DAPP) by reacting a F-labeled DAPP with 4-fluorobenzoyl chloride in the presence of silver triflate (FIG. 26A), thereby producing a DAPP having one or more reactive handles (II-13). By using 19F-NMR and a fluorine in the polymer backbone as a reference, we can monitor the
amount of trifluoromethylbenzyl that is attached to the backbone (see, e.g., FIG. 26B). Any useful reaction conditions can be modified to increase yield. For instance, reaction temperatures can be increased (e.g., of from about 60°C or greater, such as of from about 60°C to about 140°C); solvent or solvent mixtures can be modified (e.g., by use of no solvent or by use of solvents with low donor numbers, e.g., ethers, acetone, aprotic solvents, non-polar solvents, polar aprotic solvents, etc.); and concentration of reactants can be altered to maximize yield and/or selectivity.

The synthetic protocol is provided in FIG. 26A and was conducted as follows. Two g of F-labeled DAPP (2.59 mmol) was dissolved in 20 mL of methylene chloride, and 1.63 g of 4-fluorobenzyl chloride (10.3 mmol) was added to this yellow solution. The yellow solution was cooled in an ice bath, and 2.64 g of silver triflate (10.3 mmol) was added in one addition to give a dark brown color. After 1 hour, the ice bath was removed; and the reaction was stirred overnight at room temperature. Next day, the solution was added to water and heated to boil off the organic solvent. The remaining solid was then collected, rinsed with water several times, and dried in a vacuum oven overnight at 60°C.

The resultant product was dissolved in D-chloroform for 19F-NMR analysis to determine fluorine quantitative incorporation (FIG. 26B). The signal at ~105 ppm arose from the pendant fluorine on the carbonyl aryl group, while the peak at ~115 ppm corresponded to a backbone fluorine. Using the peak at ~115 ppm as a reference signal, we estimated that about 2.6 percent aryli fluoride groups were functionalized per repeat group.

The aryli fluoride group can serve as a reactive handle, which can be further reacted with other functional groups. In particular, the functional versatility of attaching the 4-fluorobenzyl group is the liability of aryl halides in the presence of a strong electron withdrawing group towards nucleophilic aromatic substitution (SnAr2). As seen in FIG. 26C, the labile aryl halide of the DAPP having a reactive handle (II-13) can be reacted with an aryl ether to attach the ether by way of an SnAr2 reaction, thereby forming the further functionalized DAPP polymer (II-14).

Example 4: Acylation Using an Arylsulfonyl Reagent

FIG. 27 provides another exemplary reagent to provide a functionalized DAPP polymer. As described herein, the reagent to provide the reactive handle can have the formula R<sup>H</sup>X, in which R<sup>H</sup> can have the formula -L<sup>2</sup>-Ar<sup>H</sup> or -L<sup>2</sup>-Ak<sup>H</sup> (e.g., any described herein). In one instance, the exemplary R<sup>H</sup>—X reagent is Ar<sup>H</sup>-L<sup>2</sup>-X, in which L<sup>H</sup> is a sulfonyl and Ar<sup>H</sup> is an optionally substituted aryl. As seen in FIG. 27, the R<sup>H</sup>—X agent includes a linker L<sup>H</sup> that is sulfonyl (—SO<sub>2</sub>—) and an aryl group Ar<sup>H</sup> that is a fluorinated phenyl. The Ar<sup>H</sup> group can serve as an Ar<sup>H</sup> group (e.g., an aryl group including a cationic moiety or a halo).

The reactive handle R<sup>H</sup> can be installed in any useful manner. In one instance, R<sup>H</sup> can be reacted with the F-labeled DAPP in the presence of a metal salt, e.g., M(OTf), a metal triflate salt. The metal triflate can promote the Friedel Crafts aroylation reaction, thereby providing an exemplary DAPP polymer (II-15) having one or more R<sup>H</sup> groups appended to the pendant aryl groups and/or the backbone aryl groups of the DAPP polymer.

Example 5: Synthesis of the Fluorinated Diels-Alder Poly(Phenylene) F-DAPP (3*)

FIG. 28 provides the first step for a synthetic scheme, which provides a fluorinated Diels-Alder poly(phenylene) F-DAPP (3*). To 16.9 g of bis[tetacycylene] (24.5 mmol) (1*) and 3.5 g of 1,4 diethynyl-2-fluorobenzene (24.5 mmol) (2*) in a 500 mL three neck round bottom flask was added 250 mL of diphenyl ether. The reaction vessel was heated to 165°C under N<sub>2</sub>. After 24 hours, the reaction vessel was cooled; and the orange, viscous medium was precipitated from acetone. The solid was isolated, dried, and dissolved in toluene (10 mL of toluene per gram) and then re-precipitated from acetone. The resultant powder was isolated and dried in a vacuum oven at 150°C for 48 hours, thereby providing F-labeled DAPP (3*).

Example 6: Acylation of Diels-Alder Poly(Phenylene) Backbone with Silver Triflate

FIG. 28 also provides the second step for a synthetic scheme, which provides a Diels-Alder poly(phenylene) having a reactive handle composed of a fluorinated acyl group (II-16). Under N<sub>2</sub>, 2 g of the fluorinated Diels-Alder poly (phenylene) (3*) (2.6 mmol) was dissolved in 150 mL of 1,2-dichloroethane in a 500 mL three neck round bottom flask. At room temperature, 2.4 g of 4-fluorobenzyl chloride (15.2 mmol) and 3.9 g of AgOTf (15.2 mmol) were added to the reaction vessel. The color of the solution changed from an initial yellow solution to a dark red solution. The reaction was heated to 50°C for 16 hours. The resultant slurry was filtered by passing through a 2 µm glass fiber syringe frit to remove excess AgOTf and AgCl. The red solution was then precipitated from reagent ethanol and dried in a vacuum oven at 150°C for 24 hours to provide a fluorooctylated DAPP compound (II-16).

Other Embodiments

All publications, patents, and patent applications mentioned in this specification are incorporated herein by reference to the same extent as if each independent publication or patent application was specifically and individually indicated to be incorporated by reference.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and that this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the invention and including such departures from the present disclosure that come within known or customary practice within the art to which the invention pertains and may be applied to the essential features hereinafter set forth, and follows in the scope of the claims.

Other embodiments are within the claims.

The invention claimed is:

1. A composition comprising a structure having the formula (I):
8. The composition of claim 1, wherein:

- at least one R′ is -L′-Ar′ and/or -L′-Ak′, or a salt thereof or a form thereof including a counter ion;
- L′ is a covalent bond, carbonyl, oxy, thio, azo, phosphonyl, phosphoryl, sulfonyl, sulfanyl, sulfonamide, imino, imide, phosphine, nitride, optionally substituted C_{1-12} alkyne, optionally substituted C_{1-12} alkylenoxy, optionally substituted C_{3-12} heteroalkylene, optionally substituted C_{3-12} heteroalkyleneoxy, optionally substituted C_{4-18} arylene, or optionally substituted C_{4-18} aryleneoxy;
- Ar′ is an optionally substituted aryl comprising the cationic moiety or the halo; and
- Ak′ is an optionally substituted alkyl comprising the cationic moiety or the halo; or an optionally substituted heteroalkyl comprising the cationic moiety or the halo.

9. The composition of claim 8, wherein L′ is a covalent bond, carbonyl, sulfonyl, SO_2, NR_2, or -CR_2=O-,

- (NR_2)SO_2-,
- NR_2-,
- (NR_2)SO_2-,
- CR_2=O-,
- (NR_2)SO_2-,
- CR_2=O-,
- (NR_2)SO_2-,
- NR_2-,
- (NR_2)SO_2-,
- CR_2=O-,
- (NR_2)SO_2-,
- CR_2=O-,
- (NR_2)SO_2-,

wherein each of R′ is independently, H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted alkyl, optionally substituted alkyl aryl, or optionally substituted aryl, or a salt thereof or a form thereof including a counter ion;

10. The composition of claim 9, wherein the composition comprises a structure having any one of formulas (Ia) to (Ii), or a salt thereof or a form thereof including a counter ion, and wherein R′ is R′ comprising the cationic moiety or R′ comprising the halo.

11. The composition of claim 1, wherein:

- R′ is -SO_2-NR_2-,
- -SO_2-,
- -NR-,
- -SO_2-,
- -SO_2-,
- -SO_2-,
- -SO_2-,
- -SO_2-,
- -SO_2-,
- -SO_2-,

wherein each of R′ is independently, H, optionally substituted alkyl, optionally substituted haloalkyl, optionally substituted alkyl, optionally substituted alkyl, or optionally substituted aryl, or a salt thereof or a form thereof including a counter ion, and wherein R′ is R′ comprising the cationic moiety or R′ comprising the halo.

6. The composition of claim 1, wherein at least one R′ is an optionally substituted C_{1-12} alkyne, optionally substituted C_{3-12} heteroalkylene, optionally substituted C_{4-18} arylene, or optionally substituted C_{4-18} aryleneoxy.

7. The composition of claim 6, wherein each and every R′ comprises an optionally substituted aryl group.
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\(R^G\), is, independently, oxy, optionally substituted alkylene, or optionally substituted heteroalkylene; and
\(R^D\) is optionally substituted aryloyl, carboxylaldehyde, optionally substituted alkanoyl, or optionally substituted alkyl.

12. The composition of claim 1, wherein \(Ar^f\) and/or \(Ar^d\) is optionally substituted phenylene, optionally substituted naphthylene, or optionally substituted phenanthrylene.

13. The composition of claim 12, wherein the optional substitution for \(Ar^f\) is \(R^F\), \(R^D\), \(R^C\), \(R^B\), or \(R^E\); and wherein the optional substitution for \(Ar^d\) is \(R^D\), \(R^C\), \(R^P\), \(R^B\), or a label.

14. The composition of claim 1, wherein the composition comprises a structure having any one of formulas (I-1) to (I-8), (IV-3), (IV-5), (IV-8), (IV-10), or (IV-11), or a salt thereof or a form thereof including a counter ion;

wherein each and every \(R^{F1}\), if present, comprises the cationic moiety or the halo;
wherein each and every \(R^{A1}\), if present, comprises the cationic moiety;
wherein each and every \(R^{F1}\), if present, comprises the halo;
wherein \(L^f\) is a covalent bond, carbonyl, oxy, thio, azo, phosphonoyl, phosphoryl, sulfonyl, sulfanyl, sulfonamide, imino, imine, phosphinic, nitrilo, optionally substituted \(C_{1-12}\) alkylene, optionally substituted \(C_{1-12}\) alkyleneoxy, optionally substituted \(C_{1-12}\) heteroalkyleneoxy, optionally substituted \(C_{1-12}\) heteroalkylene, optionally substituted \(C_{1-12}\) heteroalkyleneoxy, optionally substituted \(C_{1-12}\) heteroaryleneoxy, and optionally substituted \(C_{1-12}\) aryleneyoxy; and wherein \(m\) is an integer of from about 1 to 500.

15. The composition of claim 14, wherein:
\(R^{F1}\) is the halo, an optionally substituted aryl having the halo, an optionally substituted alkyl having the halo, or an optionally substituted heteroaryl having the halo; and/or
\(R^{A1}\) is the cationic moiety, an optionally substituted aryl having the cationic moiety, an optionally substituted alkyl having the cationic moiety, or an optionally substituted heteroaryl having the cationic moiety.

16. A composition comprising a structure having the formula (VI) or (VII):

or a salt thereof or a form thereof including a counter ion, wherein:
each and every \(R^{F1}\) comprises a cationic moiety or a halo, wherein at least one \(R^{F1}\) is an aryl, an alkyl, or a heteroaryl substituted with the cationic moiety; wherein at least one \(R^{F1}\) is an aryl, an alkyl, or a heteroaryl substituted with the halo; and wherein each of the pendant aryl groups in formula (VI) or (VII) is substituted with \(R^{F1}\);
each \(R^f\) and \(R^d\) is, independently, \(H\), halo, optionally substituted \(C_{1-12}\) alkyl, optionally substituted \(C_{1-12}\) heteroaryl, optionally substituted \(C_{1-12}\) heteroalkylene, optionally substituted \(C_{1-12}\) heteroaryleneoxy, optionally substituted \(C_{1-12}\) heteroaryleneoxy, optionally substituted \(C_{1-12}\) heteroaryleneoxy, or substituted \(C_{1-12}\) heteroaryleneoxy; and wherein each \(q\) is, independently, a bivalent linker comprising optionally substituted arenylene; each \(Ar^f\) is, independently, a bivalent linker comprising optionally substituted arenylene; each \(Ar^d\) is, independently, a bivalent linker comprising optionally substituted arenylene; each \(q\) is, independently, an integer of from 0 to 5; each \(a\) is, independently, an integer of from 0 to 5, wherein at least one \(b\) is not 0; each of \(m\) and \(n\) is, independently, an integer of from about 1 to 1000;
\(L^f\) is a sublink;
\(Ar^f\) is a hydrophobic segment; and each \(R^f\) is, independently, a reactive end group.

17. The composition of claim 16, wherein \(L^f\) comprises a covalent bond, optionally substituted \(C_{1-12}\) alkyleneoxy, optionally substituted \(C_{1-12}\) heteroalkyleneoxy, optionally substituted \(C_{1-12}\) heteroalkyleneoxy, optionally substituted \(C_{1-12}\) heteroaryleneoxy, optionally substituted \(C_{1-12}\) aryleneyoxy, optionally substituted \(C_{1-12}\) aryleneyoxy, optionally substituted \(C_{1-12}\) aryleneyoxy, or a structure of formula (II).

18. The composition of claim 16, wherein \(R^f\) is optionally substituted \(C_{1-12}\) aryl, or optionally substituted \(C_{1-12}\) aryl.

19. The composition of claim 16, wherein the composition comprises a structure having the formula (VIa) to (VIIa), or a salt thereof or a form thereof including a counter ion; or the formula (VIII) or (VIIa), or a salt thereof or a form thereof including a counter ion.

20. An anion exchange membrane comprising the composition of claim 1.